FLAME RETARDATION OF POLYMERS.

KIANG, JOSEPH KAI-YUEN

DEGREE DATE: 1979

*MSG DI4 DROLS PROCESSING - LAST INPUT IGNORED

--   1   OF   1
--   ***DTIC DOES NOT HAVE THIS ITEM***
-- 1 - AD NUMBER: D430950
-- 6 - UNCLASSIFIED TITLE: FLAME RETARDATION OF POLYMERS,
--10 - PERSONAL AUTHORS: KIANG,J. K. Y. ;
--11 - REPORT DATE: FEB   , 1979
--12 - PAGINATION: 239P
--20 - REPORT CLASSIFICATION: UNCLASSIFIED
--21 - SUPPLEMENTARY NOTE: DISSERTATION SUBMITTED TO UNIV. OF
--   MASSACHUSETTS IN PARTIAL FULFILLMENT OF PH.D.
--22 - LIMITATIONS (ALPHA):   APPROVED FOR PUBLIC RELEASE; DISTRIBUTION
--   UNLIMITED. [redacted]
--33 - LIMITATION CODES: 1 [redacted]
--******
--   END OF DISPLAY LIST

--   ((ENTER NEXT COMMAND))

INFORMATION TO USERS

This was produced from a copy of a document sent to us for microfilming. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the material submitted.

The following explanation of techniques is provided to help you understand markings or notations which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting through an image and duplicating adjacent pages to assure you of complete continuity.

2. When an image on the film is obliterated with a round black mark it is an indication that the film inspector noticed either blurred copy because of movement during exposure, or duplicate copy. Unless we meant to delete copyrighted materials that should not have been filmed, you will find a good image of the page in the adjacent frame.

3. When a map, drawing or chart, etc., is part of the material being photographed the photographer has followed a definite method in "sectioning" the material. It is customary to begin filming at the upper left hand corner of a large sheet and to continue from left to right in equal sections with small overlaps. If necessary, sectioning is continued again—beginning below the first row and continuing on until complete.

4. For any illustrations that cannot be reproduced satisfactorily by xerography, photographic prints can be purchased at additional cost and tipped into your xerographic copy. Requests can be made to our Dissertations Customer Services Department.

5. Some pages in any document may have indistinct print. In all cases we have filmed the best available copy.

7912692

KIANG, JOSEPH KAI-YUEN
FLAME RETARDATION OF POLYMERS.

UNIVERSITY OF MASSACHUSETTS, PH.D., 1979

FLAME RETARDATION OF POLYMERS

A Dissertation Presented

By

Joseph Kai-Yuen Kiang

Submitted to the Graduate School of the
University of Massachusetts in partial fulfillment
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

February 1979

Polymer Science and Engineering

FLAME RETARDATION OF POLYMERS

A Dissertation Presented

By

Joseph Kai-Yuen Kiang

Approved as to style and content by:

James C. W. Chien

Prof. James C. W. Chien, Chairman of Committee

Robert W. Lenz

Prof. Robert W. Lenz, Member

Peter C. Uden

Prof. Peter C. Uden, Member

Marcel Vanpee

Prof. Marcel Vanpee, Member

William J. MacKnight

Prof. William J. MacKnight, Head
Polymer Science and Engineering

DEDICATION

To my late grandfather, Mr. C. Y. Lee, who had loved me since the day I was born.

Old grandpa never dies, in my memory he LIVES!

ACKNOWLEDGMENTS

I wish to thank the faculty members of the Polymer Science and Engineering Department for their teaching and especially to Professor James C.W. Chien for his inspiration and direction of this work.

Thanks are also due Professors Lenz, Vanpee, and Uden for serving as committee members. A special note of gratitude is extended to Professor Uden and his research group for their assistance and invaluable suggestions in the analytical aspects of this work.

I also wish to thank Professor L.C. Dickinson and all my friends in Professor Chien's group for their fellowship in making my sojourn at UMass all the more pleasant.

My sincere gratitude goes to my parents and my wife, Shirley, for their encouragement and unending love throughout the course of this work.

Financial support in the form of a research assistantship is gratefully acknowledged.

ABSTRACT

Flame Retardation of Polymers

(November 1978)

Joseph K.Y. Kiang, B.S.Ch.E., Chung Yuan College of Science & Engineering

M.S., Lowell Technological Institute

M.S., University of Massachusetts

Ph.D., University of Massachusetts

Directed by: Professor James C.W. Chien

The central purpose of this study is to understand the chemical events that may be occurring in the decomposition of a polymer and how a potential flame retardant would in general suppress, alter or modify certain chemical reactions.

Chromyl chloride(CrO_2Cl_2) was used to react with semi-crystalline isotactic polypropylene in an Etard reaction under different experimental conditions. The chromium-containing polypropylene and the neat polypropylene were investigated for their thermal stabilities and ignition characteristics by thermogravimetric analysis(TGA) and differential thermal analysis(DTA). The relative flammabilities of these polymers were studied by the limiting oxygen index(LOI) test. In inert atmosphere, the chromium-containing polymer decomposed faster than polypropylene and exhibited a lower activation energy (44 Kcal $mole^{-1}$ vs 51 Kcal $mole^{-1}$). In oxidative environment, the former polymer inhibited decomposition by in-situ char formation resulting in a higher activation energy than the latter polymer (26 Kcal $mole^{-1}$ vs 16 Kcal $mole^{-1}$). The ignition temperature of the former polymer in air, as shown by the DTA ignition exotherm, was 150°C higher

than for neat polypropylene. A LOI of 26.4 was found for the chromium-containing polypropylene, the role of chromium and chlorine in flame inhibition is believed to be due to free radical scavenging, thus stopping flame propagation. A similar study on polypropylene found a LOI of 17.4.

A novel interfaced pyrolysis gas chromatographic peak identification system was used to pyrolyze the above polymers in inert and in oxidative atmospheres. The processes followed first-order reaction kinetics. Pyrolytic products were separated by temperature programmed gas chromatography and identified on-the-fly by rapid scan vapor phase infrared spectrophotometry, mass spectrometry, mass chromatography, and vapor phase pyrolysis. The presence of chromium in polypropylene was found not to affect the nature of the products produced. Mechanisms of product formations were proposed. In inert atmosphere, a mechanism involving intramolecular chain transfer processes, especially those of the secondary alkyl radicals, could account for the formations of most of the products. In oxidative environment, the formations of the major oxygenated products were diffusion controlled as a function of oxygen concentration. Mechanisms involving C-C scissions of the terminal and backbone alkoxy radicals accompanied by H· and ·CH_3 transfers were responsible for product formations.

Similar experiments were performed on polyisoprene and vanadium-containing polyisoprene. The latter polymer was prepared by reacting vanadium oxytrichloride($VOCl_3$) with polyisoprene hydroxylated with controlled amount of peracetic acid. The thermal stability of the above

polymers was about the same in inert atmosphere, an activation energy of about 40 Kcal $mole^{-1}$ was found for both of the polymers. In oxidative environment, vanadium also inhibited decomposition by in-situ char formation resulting in a higher activation energy than neat polyisoprene (50 Kcal $mole^{-1}$ vs 27 Kcal $mole^{-1}$). The ignition temperature of the metal-containing polymer was 100°C higher than the neat polymer under similar experimental conditions.

Pyrolysis and oxidative pyrolysis of these two polymers followed first-order reaction kinetics. The products were identified by mass spectrometry. The presence of vanadium in polyisoprene was also found not to affect the nature of the products produced. Although the thermal stability in terms of weight loss of the two polymers was about the same in inert atmosphere, product distributions, however, were very different. In oxidative environment, all of the major products were suppressed.

In inert atmosphere, a simple mechanistic scheme was proposed which involved α and β scissions of the polyisoprene chain to account for all of the products. The allylic radicals, formed from β scissions, however, were mainly responsible for product formations. Finally, similar mechanisms could be written for polyisoprene as those proposed for polypropylene in oxidative environment.

TABLE OF CONTENTS

LIST OF FIGURES

Figure

Chapter III

Chapter IV

Chapter V

Figure

Chapter VI

Figure

Chapter VII

Chapter VIII

Chapter IX

LIST OF TABLES

CHAPTER I

PRINCIPLE OF FLAME RETARDATION

Introduction

Human beings learned from time immemorial that fire can bring much human and economic misery. Fire ranks third as the most frequent cause of fatal accidents in the United States, exceeded only by motor vehicles accidents and falls. The National Fire Protection Association estimated that fires, not including those from motor vehicles, killed about 8,800 people in the U.S., and injured 108,000 in 1976. In terms of property loss, it costed about $3.4 billions. In relation to this, polymer flammability has been recognized as an increasingly important social, legal and scientific problem.

The flammability characteristics of natural and synthetic polymeric materials is of broad interest with particular aspects including coatings, fibers and fabrics, reinforced plastics, elastomers, cellular plastics, and ablative materials. Rapid expansion of plastics in wearing apparel, draperies, carpeting, automotive and aircraft components, and in allied consumer industries, makes it imperative that a better understanding of the flammability characteristics of polymers be gained.

The first federal legislation relating to combustible synthetic materials goes back to 1953 when Congress passed the Flammable Fabrics Act. In 1967, Amendment to the Act included all wearing apparel and interior furnishings. Responsibility for the Act was shifted from the Department of Commerce and the Federal Trade Commission to the Consumer Product Safety Commission when it began operation in 1973. Over the years,

the Department of Commerce's National Bureau of Standards has developed flammability tests that companies must use to determine whether their products meet federal safety specifications. In addition, federal, state and city, and some major industries have established buying specifications for materials that are potentially flammable[1].

Among the general public, considerable confusion exists about the definitions of the terms 'flame retardant', 'flame resistant', 'fire retardant', and 'fireproof'. 'Flame retardant' and 'flame resistant' are used as modifying phases to describe the property of resisting fire. 'Flame retardant' itself is also used in the nominative sense to describe a chemical species which enables a material to resist burning when exposed to a relatively low-energy ignition source, such as cigarette, match, candle or stove burner. A 'fire retardant', on the other hand, causes a material to resist burning when subjected to a high-energy ignition source, such as a flaming pool of gasoline. The term 'fireproof' is rarely used because nothing can be totally immune from the effects of a huge, raging fire. The properties of a fireproof material should not be affected by a fire. For example, steel is not fireproof, it softens near 540 °C and yields under stress at high temperatures although it is not necessarily consumed in a fire, yet important properties are destroyed. Thus, the terms, 'retard' and 'resist' imply a partial but not complete barrier to fire, whereas 'proof' is an absolute term.

Flame retardants have been known since ancient times. The early Egyptians used various inorganic chemicals, such as clay, to make woven cotton flame retardant. Solutions of alum were used to make wooden towers retardant or resistant to fire in Greece in 83 B.C. In 1683, clay and gypsum were first used to make canvas scenery in theaters flame resistant.

In 1735, Obadiah Wyld in England was granted a patent for treating cellulosic materials with a flame retardant mixture of alum, ferrous sulfate and borax. French chemist Joseph Louis Gay-Lussac in 1821 developed a flame-retardant mixture of ammonium phosphate, ammonium chloride, and borax for treating linen and jute fabrics. Durable flame retardant for fabrics consisting of stannic oxide was devised in England in 1902. In the 1930's, scientists began developing flame retardant mixtures containing metal oxides or salts, together with chlorinated organic compounds, for treating cotton. One such mixture consisted of antimony trioxide suspended in chlorinated paraffins or polyvinyl chloride.

It should be pointed out that the science of flame retardation originated from the investigations of the ease of ignition of natural materials such as cotton and jutes in early days. This is the reason why most of the early reported studies and patents were concerned with these materials. With the advent of synthetic polymers and their increased acceptance by the general public, the study of flame retardation of these materials has become necessary.

Among the synthetic polymers, relatively little attention has been paid to the flammability of elastomers. Even though the ignition and burning characteristics of rubbers are a matter of some concern in a few specific applications, the total volume of rubber used in these applications is rather small and consequently, research in this area lags behind the corresponding efforts given to plastics. However, the rapid increase in the use of elastomers in many consumer oriented applications has recently caused a greater emphasis to be placed in the flammability behavior of these materials. The recently formed Committee 39 of the ASTM (American

Society for Testing and Materials) has been charged with the responsibilities of establishing the criteria necessary to design tests for the flammability of these materials.

Flame Retardation of Synthetic Polymers

The rapidly growing demands for synthetic polymers and the increasing public awareness of their potential as fire hazards have revived the old problem of flammability which has been exhaustively studied for natural polymers such as cotton and jute.

The goal in this area is the flame retardation of polymers and not their flame proofing. Mark et al.[2] had established a number of guidelines for an ideal flame retardant polymeric system. This system should have 1) a high resistance to ignition and flame propagation, 2) a low rate of pyrolysis, 3) a low rate and amount of smoke generation, 4) low combustibility and toxicity of combustion gases, 5) retention of reduced flammability in appearance and properties for specific end-use, and 7) little or no economic penalty. Therefore, a flame retardant system, in addition to being formulated from efficient, economic chemicals, should require no unusual processing conditions, must be applicable in commercial equipment, and must be durable under all use conditions. All of these requirements dictate the type of evaluation necessary for flame retardant systems.

Flame retardation is essentially an interruption of the burning process. In most cases, only vapor phase materials can truly burn. Condensed phase materials(liquids and solids) have to be converted to the vapor phase before ignition and combustion can occur. Thus, the majority of synthetic polymers such as plastics and fibers, under typical fire exposure

conditions, contribute significantly to the vapor phase which is potentially flammable. Reducing the flammability of a solid material can therefore be divided into two phases: reducing the degrees of conversion into vapor phase materials, and changing the vapor phase materials into less flammable ones[3].

To know how flame retardants can reduce the degree of conversion of a solid polymer into vapor phase materials and/or change the latter into less flammable ones, an understanding of the thermal and thermoxidative decomposition of the polymer is essential. The study of the thermal decomposition of a polymer in an inert atmosphere usually precedes those of the more complex thermoxidative decomposition in an oxidizing environment. This information may help one to make an initial judgment as to the general behavior of this polymer in the presence of a heat source. For example, a polymer such as polymethylmethacrylate which undergoes a facile thermal depolymerization to produce combustible monomer, is considered to be less flame retardant than polyvinyl chloride, which produces the non-combustible hydrogen chloride vapor. However, more practical information can be obtained by studying the thermoxidative decomposition in environment similar to those encountered in an actual fire situation. The rate of thermoxidative decomposition of a polymer depends on the prevailing temperature of the environment.

It is well known that molecular oxygen, because of its high reactivity towards possibly present free radicals, causes the formation of hydroperoxide groups, -OOH. As a result of the lability of the peroxide bond, these hydroperoxides tend to decompose with the formation of new free radicals which, in turn, again form hydroperoxides. Thus, the reaction becomes autocatalytic.

The formation of hydroperoxide groups creates the prerequisites for oxidative decomposition of the polymer because the free radicals, formed by decomposition of these groups, can lead to chain scissions. At temperatures below about 200°C, halogenated flame retardants(stabilizers), are usually used to interfere with the earliest preignition processes, namely, formation of active chain radicals, chain decomposition, and the generation of combustible volatile products. Table 1 shows some examples of commercially used flame retardants. However, at temperatures about 250°C, the rate of the chain scissions increases rapidly owing to the accelerated formation of active free radicals, the above flame retardants(stabilizers) will no longer be capable of slowing these reactions and other types of flame retardants are required to suppress polymer combustion. These flame retardants include those which produce nonflammable gases; those which incorporate inorganic materials; and those which form char. Examples of these flame retardants have been reported by Mark et al.[2].

The noncombustible gases are very desirable diluents for combustible decomposition products such as HCHO, CH_3CHO and low molecular weight hydrocarbons. In addition to gas phase dilution, the water released from flame retardants containing, for example, hydrated alumina is associated with an energy loss due to the endothermic dehydration and evaporation processes. Finely powdered inorganic fillers increase the thermal conductivity of the system and slow the rate of temperature increase, thus suppressing the ignition of the polymer. Finally, char formation prevents further access of oxygen and forms a solid, immobile residue instead of a liquid burning mass.

In general, five speculative modes of action have been proposed for flame retardation of polymers[2].

Table 1

Examples of Commercial Flame Retardants[2]

Trade Name	Composition or Structure
(a) Halogen-rich, organic Flame Retardants	
Chlorowax	Chlorinated paraffin
DER	Brominated Epoxy resin
Tetrabromo-bisphenol A	$C(CH_3)_2(C_6H_2Br_2OH)$
Firemaster PHT 4	Tetrabromo-phthalic anhydride
Firemaster BP4A	Tetrabromo-bisphenol A
Firemaster 5BT	Pentabromotoluene
BP-10	Decabromobiphenyl
Aroclor 5442 & 5460	Chlorinated triphenyl
Hexachlorocyclopentadiene	C_5Cl_6
Dechlorane 510 & 4070	$(C_5Cl_6)_2$
EB-80	Pentabromoethylbenzene
(b) Miscellaneous Flame Retardants	
Antimony oxide	Sb_2O_3
Diammonium phosphate	$(NH_4)_2HPO_4$
Zinc borate	$Zn(BO_2)_2$
C-30 BF	$Al_2O_3 \cdot 3H_2O$
Ammonium bromide	NH_4Br
Fyrol 32-B	$(BrCH_2CH_2Br\text{-}CH_2\text{-}O)_3PO$
TPP	Triphenylphosphite, $P(O\text{-}C_6H_5)_3$
Triphenylphosphine oxide	$OP(C_6H_5)_3$

Gas Theory

Generation of noncombustible gases which dilute the flame oxygen supply and tend to exclude oxygen from the polymer surface.

Thermal Theory

Radicals or molecules from retardant decomposition react endothermically with flame species or substrate species and retardant decomposes endothermically.

Chemical Theory

Retardant decomposes into free-radical acceptors which interfere with flame chain reactions.

Coating Theory

Nonvolatile char is formed which minimizes the oxygen diffusion to the condensed phase and also reduces the heat transfer from the flame to the polymer.

Physical Interaction Theory

Finely divided particles or solid interfaces may form endothermically and lower the net heat of combustion or reduce flame propagation by altering the course of gas phase reactions and lead to less active radicals.

It should be pointed out that the above proposed theories do not contradict, but rather complement, each other.

How Flame Retardants Work

The question of how various flame retardants work to inhibit burning is still, in some cases, highly controversial. In general, flame retardation is believed to result from the presence in the retardant of one or more key elements, such as phosphorus, nitrogen, chlorine, or bromine, or of a volatile compound, such as water of hydration. This section discusses some of the more commonly held theories about how some of these substances function to suppress polymer combustion.

Phosphorus

Phosphorus acts primarily in the solid phase and is believed to function as a flame retardant by a variety of mechanisms. Probably the most important is its ability to increase markedly the conversion of organic matter to char during burning and thus to decrease the formation of flammable carbon-containing gases. Combustion is inhibited because the char does not burn readily and because the amount of combustible gases, such as hydrocarbons, is greatly reduced. By its char formation, phosphorus restricts oxygen access and consequently directs carbon oxidation to CO rather than to CO_2. The CO formation has the advantage of 70 Kcal $mole^{-1}$ lower exotherm than CO_2 formation[4].

Phosphine oxides, phosphonic acids, and phosphinic acids were found to be flame retardants for various thermoplastics. It was postulated that the acidity of the compounds was directly related to their activity and that the formation of polyphosphates(or phosphate glasses) was vital to the mechanism by which they functioned[5]. The use of phosphate flame retardants on cotton has been well documented[6]. It is believed that these

compounds inhibit burning by producing phosphoric acid, which promotes char formation and retards the decomposition of cellulose to combustible tar, aldehydes and ketones. The mechanisms of flame retardation with phosphorus compounds were reported by Lyons[7].

Nitrogen

The role of nitrogen in flame retardants is poorly understood. It is suggested that nitrogen probably is a flame retardant element in some forms, however, it is not very efficient. Lyons[7] suggested that in the presence of phosphorus compounds, nitrogen compounds probably acted in two ways as flame retardants. Nitrogen acids could form (e.g., HNO_2, HNO_3) and aid in char formation by promoting formation of carbonium ions (vide supra). Nitrogen compounds in various oxidation states could volatilize and inhibit flaming combustion by serving as free radical traps.

Chlorine and Bromine

The two elements are believed to work mainly in the gas phase. Among other things, these halogens remove from the flaming gas the hydrogen free radicals that, along with both oxygen free radicals and hydroxyl free radicals, are essential to sustaining the combustion process.

If the flame retardant is a bromine compound, for example, the burning causes it to release gaseous hydrogen bromide. The hydrogen bromide then apprently reacts with the hydrogen free radicals to form molecular hydrogen gas and bromine free radicals. Hydrogen free radicals and bromine free radicals combine to regenerate hydrogen bromide. Both of these reactions remove hydrogen free radicals from the flaming gas and thus suppress the burning process.

$$HBr + H\cdot \rightarrow H_2 + Br\cdot \qquad (1)$$
$$H\cdot + Br\cdot \rightarrow HBr$$

Similar reactions may take place to remove oxygen free radicals and hydroxyl free radicals from the burning gas. For example, hydrogen bromide may react with hydroxyl free radicals to form water and bromine free radicals, thus reducing the hydroxyl free radical concentration.

$$HBr + OH\cdot \rightarrow H_2O + Br\cdot \qquad (2)$$

Hydroxyl free radicals are important to combustion because they can react with CO to form CO_2 and hydrogen free radicals. This reaction, being exothermic, is believed to play a significant role in sustaining the burning process.

The role of chlorine is very similar to that of bromine. Comparing bond energies, the relative effectiveness of halogens is HBr ≈ HI > HCl >> HF. HBr is more effective than HCl in flame retardation because the former has a lower bond energy. HI is not commonly used because of cost consideration. HF, on the other hand, is not effective at all because of its strong bond.

Antimony Compounds

The most important compounds in this category are the trioxide(Sb_2O_3) and the oxychloride(SbOCl). The trioxide by itself is a very poor flame retardant. However, when used in conjunction with a halogenated organic compound the system is very effective. If HCl gas is released from the halogenated compound, then it reacts with the solid Sb_2O_3 to form $SbCl_3$ which then reacts with both hydrogen free radicals and hydroxyl free radicals. The resulting removal of these free radicals interferes with

combustion and can cause the flame to be extinguished.

A number of mechanisms have been suggested to account for the mode of flame retardation of $SbCl_3$. One suggests[8] that trivalent antimony facilitates generation of halogen radicals with resulting interference to the normal free radical mechanism of flame propagation. Another suggests[9] that the formation of $SbCl_3$ and/or SbOCl simply delays the rate of escape of the halogen from the flame and thus increases the chance of reaction with the propagating species. Yet another suggests[10] that volatile $SbCl_3$ acts by blanketing the flame. Finally, char formation in the solid phase has also been suggested as one of the mechanisms since $SbCl_3$ and/or SbOCl can act as dehydrating agents in the pyrolysis of cellulose[11].

Alumina Trihydrate ($Al_2O_3 . 3H_2O$)

This compound suppresses burning in a number of ways. When heat is applied to a material containing this compound, the temperature rise is slowed down because the trihydrate absorbs heat when the temperature reaches about 220° to 230°C, the alumina trihydrate decomposes into anhydrous alumina and water endothermically. The water vapor dilutes and cools the combustible gases and retards their burning.

Boron

Not much is known about how boron, often used in the form of boric acid or borax, acts as a flame retardant. Like phosphorus, it acts primarily in the solid phase where it promotes char formation and inhibits the release of combustible gases from the burning material.

Synergism

Practical experience has led to the recognition that combinations of flame retardants frequently are the best means for achieving flame retardation. A synergism is defined as a situation in which the effect of two components taken together is greater than the sum of their effects taken separately. This subject has been reviewed thoroughly by Weil[12] and demonstrated kinetically by Schwarz[13]. Although not mentioned by name, two systems that have been discussed in previous sections are actually synergistic systems, they are the phosphorus-nitrogen and antimony-halogens systems.

The phosphorus-nitrogen synergism has been widely used in cellulose as evidenced by the number of published studies and patents. However, only scattered accounts of this synergistic system in polymers other than cellulose appear in the literature; the sparsity of such reports and the very limited usage of this system in other polymers suggest that this synergism is not general. On the other hand, all of the durable flame retardant finishes for cotton to date which have reached an advanced stage of development or actual commercial usage are concerned with this system. Although uncommon, the phosphorus-nitrogen synergism had been used successfully to flame-retard rigid polyurethane foams[14,15].

The interaction of antimony compounds most commonly as antimony oxide, with halogenated polymers or polymer containing halogenated additives, constitutes the classical case of synergism. Antimony oxide is usually found to be of low flame retardant activity in the absence of halogenated polymers or additives.

Pitts[16] had shown that the flame retardant effect of antimony oxide

increased as halogen was added to the system, up to an atomic ratio of three halogen atoms per antimony atom. Antimony halides had been shown to be potent flame suppressants when directly volatilized into a flame. The mechanism of an antimony-halogen synergism was proposed by Pitts et al.[17] as followed.

$$\left.\begin{array}{l}
Sb_2O_3 + 2HCl \longrightarrow 2SbOCl + H_2O \\
5SbOCl_{(s)} \xrightarrow{245^\circ-280^\circ C} Sb_4O_5Cl_2 + SbCl_3\uparrow \\
4Sb_4O_5Cl_2 \xrightarrow{410^\circ-475^\circ C} 5Sb_3O_4Cl_{(s)} + SbCl_3\uparrow \\
3Sb_3O_4Cl \xrightarrow{475^\circ-565^\circ C} 4Sb_2O_{3(s)} + SbCl_3\uparrow \\
Sb_2O_{3(s)} \xrightarrow{658^\circ C} Sb_2O_{3(l)}
\end{array}\right| \qquad (3)$$

In the presence of an halogen(e.g., chlorine) source, Sb_2O_3 formed SbOCl which decomposed in three endothermic steps through the 245°-565°C region, resulting in the evolution of $SbCl_3$ and leaving a solid Sb_2O_3. The endothermic release of $SbCl_3$, in conjunction with its blanketing effect worked together to quench the flame. In the case for polyurethane foam, the large endotherm at 245°C was believed to be particularly helpful in lowering the decomposition rate of the foam just at the point when it was beginning to accelerate and evolve flammable materials. The efficiency of this matching of the decomposition temperature between the flammable substrate and retardant additive had been cited as the key to good flame retardation, the so called 'right place at the right time' theory[10,18].

On the other hand, Sb_2O_3 alone, even up to 60 parts per hundred by weight(phr) showed little flame retardation as evidenced by the ASTM D-1692-67T flammability test. However, in another study, Martin and Price[19]

increased as halogen was added to the system, up to an atomic ratio of three halogen atoms per antimony atom. Antimony halides had been shown to be potent flame suppressants when directly volatilized into a flame. The mechanism of an antimony-halogen synergism was proposed by Pitts et al.[17] as followed.

$$
\left.
\begin{array}{lcl}
Sb_2O_3 + 2HCl & \longrightarrow & 2SbOCl + H_2O \\
5SbOCl_{(s)} & \xrightarrow{245^\circ-280^\circ C} & Sb_4O_5Cl_2 + SbCl_3\uparrow \\
4Sb_4O_5Cl_2 & \xrightarrow{410^\circ-475^\circ C} & 5Sb_3O_4Cl_{(s)} + SbCl_3\uparrow \\
3Sb_3O_4Cl & \xrightarrow{475^\circ-565^\circ C} & 4Sb_2O_{3(s)} + SbCl_3\uparrow \\
Sb_2O_{3(s)} & \xrightarrow{658^\circ C} & Sb_2O_{3(1)}
\end{array}
\right| \qquad (3)
$$

In the presence of an halogen(e.g., chlorine) source, Sb_2O_3 formed SbOCl which decomposed in three endothermic steps through the 245°-565°C region, resulting in the evolution of $SbCl_3$ and leaving a solid Sb_2O_3. The endothermic release of $SbCl_3$, in conjunction with its blanketing effect worked together to quench the flame. In the case for polyurethane foam, the large endotherm at 245°C was believed to be particularly helpful in lowering the decomposition rate of the foam just at the point when it was beginning to accelerate and evolve flammable materials. The efficiency of this matching of the decomposition temperature between the flammable substrate and retardant additive had been cited as the key to good flame retardation, the so called 'right place at the right time' theory[10,18].

On the other hand, Sb_2O_3 alone, even up to 60 parts per hundred by weight(phr) showed little flame retardation as evidenced by the ASTM D-1692-67T flammability test. However, in another study, Martin and Price[19]

had shown that triphenyl antimony alone in concentration as low as three Sb atoms per 1000 carbon atoms was an effective inhibitor for epoxy. They proposed that the triphenyl antimony vaporized and carried Sb into the flame.

Another form of synergism worth mentioning is that of the free radical initiator system. Eichhorn[20] had shown that addition of small amounts of free radical initiators such as organic peroxides to polystyrene greatly reduced the amount of a halogenated additive required to achieve a self-extinguishing rating or to reduce the self-extinguishing time to a given level. For example, 5 phr of acetylene tetrabromide was required alone to obtain a self-extinguishing rating for polystyrene. However, when 0.5 phr of dicumyl peroxide was used, only 0.5 phr of the acetylene tetrabromide was required to achieve the same self-extinguishing rating. A mechanism involving the attack of the polymer by the initiator and subsequent reaction between polymer fragments and the halogen compound was proposed. Later work by Gouinlock et al.[21] and Fenimore[22] had indicated that the observed free radical synergism might be primarily a dripping phenomenon owing to a decrease of the melt viscosity of the burning polymer. The latter worker compared two experiments in which dripping was allowed in one but not in the other. It was found that if dripping was allowed, dicumyl peroxide was effective as flame retardant whereas if dripping was suppressed, the dicumyl peroxide was not effective at all. Dripping is usually undesirable because it can act as a secondary ignition source.

The use of inorganic compounds as flame retardants and synergists is of particular interest in this study. A wide variety of metal chelates as synergists together with halogenated compounds had been used to flame-retard polystyrene[23]. For example, expanded polystyrene containing 10 percent chloroparaffin burned when ignited,but was self-extinguishing in

less than 1-2 seconds when 0.5-1 phr of the acetylacetonates of Co(III), Mo(III), Cu(II), Mn(III), or Cr(III) was used. In another patent, combination of chlorinated biphenyls or polyphenyls with finely divided copper, cuprous chloride, or cupric chloride had been shown to flame-retard silicone elastomers[24].

Finally, it should be pointed out that the combinations of flame retardants do not always show synergistic effects. Antagonistic effects may also occur. An antagonistic effect is one in which the sum of the effects of the two components taken together is less than the sum of the effects of the two components taken independently. A Celanese technical bulletin[25] had indicated that the incorporation of antimony oxide into brominated epoxy resin containing ammonium polyphosphate had an adverse effect on the flame-spread rating of the resins.

Flammability Tests

Flammability tests for polymers are designed to measure the behavior of polymers when exposed to an ignition source. These tests have been designed and modified continuously as need develops to meet new regulations. The most popular ones are listed in Tables 2 and 3.

In the testing and evaluation of flame retardants it must be remembered that, unfortunately, a flame retardant system which exhibits superior performance over another in one flammability test may not necessarily exhibit superior performance in yet another test. It is also important to remember that more than one flammability test is required to evaluate a system in the laboratory. Even after thorough laboratory evaluations have been completed, the correlation of these data with actual burning conditions may be poor. Hence, a decision to promote a flame retardant should not be based only on laboratory developmental test data.

Table 2

Some Small-Scale Flame Tests

ASTM D 635	horizontal bar
UL Subject 94	vertical (and horizontal) bar
UL Subject 758	insulated electric wire (horizontal)
UL Subject 83	insulated electric wire (vertical)
ASTM D 568	vertical film
ASTM D 1692	cellular plastics, horizontal
ASTM D 1433	SPI 45 degree test
ASTM D 2863A, B	oxygen index, self-supporting flexible plastics
ASTM D " C	oxygen index, cellular plastics
ASTM D " D	oxygen index, film or thin sheet
ASTM D 1929	hot-air ignition furnace (Setchkin)
DOT 302	automotive
ASTM D 757	electrical incandescent rod (globar)
HLT-15	Hooker's intermittent test
ASTM D 2859	pill test (tablet test), carpet & rugs DOC FF 1-70 & FF 2-70
DOC FF 4-72	mattresses
ASTM D 2843	Rohm & Haas XP-2 smoke chamber
NBS Smoke Chamber	
ASTM D 3014	rigid cellular plastics (Butler chimney test)

Table 3

Some Medium-Scale Flame Tests

ASTM E 162	radiant panel	18 x 6 inch specimen
Monsanto	2-foot tunnel	
ASTM E 286	8-foot tunnel	

Some Large-Scale Flame Tests

ASTM E 84	25-foot long tunnel (Steiner Tunnel)
ASTM E 119	building materials, fire endurance
ASTM E 152	door assemblies
ASTM E 108	roof coverings
ASTM E 163	window assemblies

In general, test methods can be divided into two classes. The laboratory developmental tests and performance tests. For example, the small-scale ASTM D 635 horizontal bar test[26] and ASTM D 2863 oxygen index test[27] belong to the first category. The former test studies the burning rate of a piece of molded plastic and the latter test examines the relative flammabilities of different polymers. The second category includes those tests such as the small-scale ASTM D 2859 pill test[28] for carpets and rugs; medium-scale ASTM E 162 radiant panel test[29] for flame-spread; and large-scale ASTM E 84 tunnel test [30], also for flame-spread.

Many small-scale tests determine the ease of ignition under specified conditions and are often used in screening work. The oxygen index test developed by Fenimore and Martin[31], is often used in the laboratory as a screening tool for materials with respect to their relative flammabilities

because of its simplicity and good reproducibility. In this test, an 80 mm long rod or strip of materials is subjected to a continuously renewed atmosphere of oxygen and nitrogen. The sample is ignited at its upper end with a pilot flame.

The limiting oxygen index(LOI) is defined as the minimum volume percent of oxygen in an oxygen-nitrogen mixture which will just permit the sample to burn in a 'candle-like' fashion[27].

$$LOI = \frac{O_2}{O_2 + N_2} \qquad (4)$$

However, this test does not take into considerations the convective heating of the sample and the turbulent mixing in the flame. While these conditions are mainly responsible for the excellent reproducibility of the test, they are also the primary cause for the lack of correlation of this test with other burning tests, which normally do include these factors. Another factor strongly influencing the outcome of LOI determination is the tendency of a sample to melt and to drip. This process carries heat away and generally leads to too high a LOI value. LOI values for some polymers are listed in Table 4. Another not so often used test similar to the oxygen index test is the nitrous oxide index test[32] in which nitrous oxide is used as the oxidant in a nitrous oxide-nitrogen atmosphere. The limiting nitrous oxide index is defined as in Equation 4 with nitrous oxide replacing the oxygen.

Very often, none of the tests listed in Tables 2 and 3 give equivalent results for any specific property. For example, flame-spread values depend strongly on sample orientation and direction of air flow relative to the direction of flame travel. The tunnel test ASTM E 84, in which both the air flow and flame travel are in the same direction, will give

Table 4

Limiting Oxygen Index (LOI) Values of Different Polymers[2]

Polymer	LOI
(a) Polymers tested as bars	
Polyethylene	17.4
Polypropylene	17.5
Polymethylene oxide	15.3
Polyphenylene oxide	28.5
Poly(2,6-dimethyl)phenylene oxide	30.5
Polystyrene	18.3
Polymethyl methacrylate	17.3
Nylon 6	23-26
Polyethylene terephthalate	22-26
Polyvinyl chloride	38-45
Polyvinylidene chloride (Saran)	60
Polyvinylidene fluoride (Kynar)	43.7
Polytetrafluoroethylene (Teflon)	95.0
Polyarylene carbonates	26-29
Polyarylene sulfones	29-31
(b) Polymers tested as fabrics	
Cellulose	18-20
Polypropylene	18
Polyethylene terephthalate	20-21

much faster flame-spread than the radiant panel test ASTM E 162, in which the two directions are opposite. Smoke generation[33,34] by burning polymeric materials in addition to those derived from the flame retardants themselves has become a factor of increasing concern in assessing materials for building and home furnishing applications. The tunnel test (ASTM E 84) and the radiant panel test (ASTM E 162) provide for determination of smoke. The former measures light absorption by means of a photometer and in the latter, the solid smoke particles are collected by filtration and weighed.

Combustion Toxicology

The problem of combustion toxicology has warranted tremendous attention in recent years. A bibliography of published information on combustion toxicology containing 47 references had been reported by Hilado[35]. Analysis of fire deaths had revealed that most of the deaths were not due to flame contact, but were a consequence of the toxicity of evolved gases from burning materials. The effect of simultaneous oxygen depletion and temperature rise is the major cause of these deaths. Unfortunately, the large number of standardized tests discussed previously for defining flammability criteria do not include biological evaluation of the effluent gases and particulates. This is a complicated matter because when standardized toxicity tests are to be considered, a very complex series of factors will come into play which can give different toxicity data from evaluation of the same materials. To this effect, MacFarland[36] had described the dilemma toxicologists faced in attempting to define the toxicity of pyrolysis products of polymers.

Conclusion

Polymer flammability is an important social and scientific problem. The expanding use of flame retardants in recent years is the result of the increase in the number of federal and state regulations, local codes, insurance underwriter regulations, and voluntary industry codes that have necessitated the use of these chemicals.

The flame retardant chemicals industry faces a multitude of challenges. One of these will be the increasing demand for effective and safe flame retardants in an ever-widening range of products. This demand will be intensified by the new regulations expected to be issued by the Consumer Product Safety Commission. Additional demand is likely to arise from new rules to be issued by the Department of Transportation, which regulates the flammability of materials used in automobiles, tanks, aircrafts and so on and by the Department of Health, Education and Welfare, which sets flammability standard for the interior materials of construction used in hospitals and nursing homes.

The federal ban on Tris (tris 2,3-dibromopropyl-phosphate), a most widely used flame retardant in polyester fabric, has caused a severe lessening of interest in additive type flame retardants, at least as far as the texile industry is concerned. Interest is shifting towards inherently flame retardant fibers. The demise of Tris has caused the producers of flame retardants in general to become more concerned than ever about the safety of their products. They are spending hundreds of thousands of dollars to determine whether a product or potential product is toxic, mutagenic, carcinogenic or otherwise harmful.

Despite the many factors tending to discourage research on new flame retardants, scientists are still attempting to find new compounds

that are more effective than existing flame retardants and especially when used in low concentrations.

Fianlly, a better fundamental understanding of polymer decomposition, the precursor to flammability, is essential to the development of new flame retardants.

References

1. 'A Guide to Today's Flammability Regulations and Tests', Flammability Institute, University of Detroit, Detroit, Mich., 48221, U.S.A.

2. Mark, H.F., Atlas, S.M., Shalaby, S.W., Pearce, E.M., Polymer News, 2, 3, 1976

3. Hilado, C.J., 'Flammability Test Methods Handbook', Chapter 1, Technomic, Conn., 1973

4. Hoke, C.E., SPE J., 29, 38, 1973

5. Sherr, A.E., Gillham, H.C., Klein, H.G., Advances in Chemistry Series, ACS, ed. by Gould, R.J., 85, 307, 1968

6. Lewin, M., Sello, S.B., 'Flame-Retardants Polymeric Materials', ed. by Lewin, M., Atlas, S.M., Pearce, E.M., Chap. 2, Plenum, N.Y., 1975

7. Lyons, J.W., 'Flammability of Solid Plastics', ed. by Hilado, C.J., 228, Technomic, Conn., 1974

8. Lindemann, R.F., Ind. Eng. Chem., 61, 70, 1969

9. Rhys, J.A., Cleaver, R.F., Plastics and Rubber Weekly, 20, Nov. 13, 1970

10. Rhys, J.A., Chem. Ind.(London), 187, Feb., 1969

11. Lyons, J.W., 'The Chemistry and Uses of Fire Retardants', 209, Wiley, N.Y., 1970

12. Weil, E.D., 'Flame Retardance of Polymeric Materials', 1, Chap. 3, ed. by Kuryla, W.C., Papa, A.J., Marcel Dekker, N.Y., 1973

13. Schwarz, R.J., 'Flame Retardance of Polymeric Materials', ed. by Kuryla, W.C., Papa, A.J., 2, p.112, Marcel Dekker, N.Y.,1973

14. Walsh, E.N., Uhing, E.H., Beck, T.M., ACS, Div. Organic Coating, Plast. Chem., Preprints, 23, 1, 1963

15. Kreutz, G.R., Jr., Kelly, D.J., (to Scott Paper Co.), Belgium Pat. 757, 421(1969)

16. Pitts, J.J., J. of Fire and Flammability, 3,57, 1972

17. Pitts, J.J., Scott, P.H., Fowell, D.G., J. Cellular Plastics, 6, 35, 1970

18. Schmidt, W.G., Trans. J. Plastics Inst., 247, December 1965

19. Martin, F.J., Price, K.R., J. App. Poly. Sci., 12, 143, 1968

20. Eichhorn, J., J. of App. Poly. Sci., 8, 2497, 1964

21. Gouinlock, E.V., Porter, J.F., Hindersinn, R.R., J. Fire and Flammability, 2, 207, 1971

22. Fenimore, C.P., Combustion and Flame, 12, 155, 1968

23. Rauschenback, R.D., Naarmann, H., Meyer, F., Ilgemann, R., (to Badische Anilin & Soda-Fabrik AG), U.S. Pat. 3,326,832 (1967)

24. Berridge, C.A., (to General Electric Co.), U.S. Pat. 3,154,515, 1964

25. Formulating Epoxy Compounds with Low Flame Spread Ratings. Technical Bulletin 0667, Celanese Resins Div. of Celanese Coating Co.

26. Am. Soc. Test. Mater., ASTM D635-60, ASTM std. 27, 200, (Jan. 1964)

27. Am. Soc. Test. Mater., ASTM D2863-70, ASTM std. 27, 727, (July, 1972)

28. U.S. Dept. of Commerce, Stand. for Surface Flammability of Carpets and Rugs, DOC FF 1-70, Fed. Regist. 35, 6211, (April 16, 1970)

29. Robertson, A.F., Gross, D., Loftus, J.J., ASTM Proc. 56, 1437, 1956

30. Steiner, A.J., UL Res. Bulletin No. 32, 1944

31. Fenimore, C.P., Martin, F.J., Mod. Plastics, 44, 141, 1966

32. Fenimore, C.P., Jones, G.W., Combustion and Flame, 10, 295, 1966

33. Nelson, G.L., J. Fire & Flammability, 5, 125, 1974

34. Hecker, K.C., Fruzzetti, R.E., Sinclair, E.A., Rubber Age, 105, 25, 1973

35. Hilado, C.J., Combustion Toxicology, 1, 91, 1974

36. MacFarland, H.N., Amer. Indust. Hyg. Assoc. J., 29, 7, 1968

CHAPTER II

HISTORICAL SURVEY OF THE APPLICATIONS OF PYROLYSIS OF POLYMERS

Pyrolysis techniques are among the oldest approaches to the study of the structure of polymeric systems. Williams[1] in 1860 isolated the basic isoprene unit by pyrolyzing natural rubber in an iron retort. Staudinger and co-workers[2,3], Midgley and Henne[4], and Bassett and Williams[5] all pyrolyzed natural rubber at temperatures between 275°-700°C and obtained different concentrations of isoprene. It was based on this discovery by the early workers that synthetic rubbers were made. It was not until World War II that scientists the world over stepped up research on synthetic rubbers that they were really concerned with pyrolysis. At that time, synthetic polymer chemistry was still in its infancy and many of the chemical and physical properties of these materials remained unknown. Among these properties, thermal stability was one of the major concerns. The object then was to establish a relationship between the structural formulae of polymers and their refractoriness under the influence of heat. The effect of double bonds and their frequency in the macromolecular chain, the size and distribution of side chains, on the number and size of fragments obtained in pyrolysis was of primary concern. In the late 1950's, the object of pyrolysis was about the same, however, more complex polymers and copolymer systems were studied. For example, the problems of branching, degree of cross-linking, blends, stereoregularity, and the presence of blocks or grafts, opened up new avenues for the applications of pyrolysis. Very often, slow pyrolysis at suitable temperatures revealed weak links by prefer-

ential fragmentation and knowledge of the subsequent products helped to improve the polymeric system studied.

Madorsky and Straus[6] found that the types and relative amounts of the pyrolysis products were functions of the molecular structure and the kind and frequency of side groups. The thermal stability and decomposition products could be related to the strengths of the C-C bonds in the polymer chain, i.e., secondary > tertiary > quaternary. Thus, pyrolysis of isotactic polypropylene yielded a lot more light hydrocarbons than polymethylene as a result of scissions at the more reactive tertiary carbon atoms[7].

Wall and Straus[8] studied the difference in the thermal decomposition behavior of linear and branched polyolefins by pyrolysis. The linear polymer exhibited behavior characteristic of a random decomposition while the branched materials did not. It was concluded that the greater the branching, provided that the branches were longer than one carbon atom, the greater was the rate of decomposition and the more it was at variance with random theory. Furthermore, polymer branching enhanced intramolecular transfer at the expense of intermolecular transfer. Similar studies with pyrolysis-gas chromatography, PGC, on high and low density polyethylenes had been reported by Kolb and Kaiser[9] and Deur-Siftar[10]. These authors reported different pyrograms for the two polymer samples. In the latter study, the increase in content of butenes with increased degree of branching was attributed to the presence of C_4 branches in the low density polyethylene. This was confirmed by Oakes and Richards[11] who had observed preferential rupture near the branching points of partially degraded low density polyethylene by infrared. Pyrolytic

preferential fragmentation had also been reported for condensation polymers especially if the polymers contained phenyl groups. PGC of phenol-formaldehyde had shown that scissions usually occurred at the side chains[12].

The principle of preferential fragmentation as observed by PGC was also used to study the tacticity of polypropylene[13]; distinguish between random and block copolymers[14, 15, 16, 17]; and determine the composition of copolymers[17,18].

Bombaugh et al.[17] had shown that random copolymers of ethylene with methyl acrylate or methyl methacrylate yielded on pyrolysis a lower ratio of methanol to methyl acrylate or methyl methacrylate, respectively, than block polymers of the same composition. Quantitative estimation of copolymer composition was obtained from gas chromatographic peak height or area ratios for peaks that were characteristic for each component. Direct comparison with calibration curves from polymers of known composition was required. Esposito[18] had demonstrated the applicability of the internal standardization technique used with PGC for the quantitative analysis of methacrylate styrene, and styrenated alkyd resins in various coating systems.

PGC offers a rapid means of analysis of volatile pyrolytic products which were often done by more time consuming separation methods[1-5]. This procedure had been used to study polymers, such as polypropylene[21-24], polyisoprene[25-31], poly(vinylchloride)[32-34], polystyrene and polyethylene[35], polybutene and poly-4-methylpentene-1[14], polyesters[36] and many others. This method had also been employed in the studies of the kinetics of polymer decomposition over wide ranges of temperatures[37]; thermal properties in the presence and absence of additives[21] and; mechanisms of polymer

decompositions[19,22,24,26]. These kinds of studies are extremely important in the investigations of flame retardation of polymers.

The growing acceptance of synthetic polymers in the 1970's in applications requiring flame retardation has prompted scientists to go back to basic research to make new high-temperature polymers or to qualify products with regard to the more and more stringent flammability standards. PGC and evolved gas analysis have played an important role in understanding the mechanisms of polymer decomposition and how potential flame retardants work to inhibit the combustion of the solid polymer or to extinguish the flame[38,39]. Furthermore, the problem of combustion toxicology has been of major concern in recent years and this problem will never be solved without detailed studies of the evolved gases from pyrolysis.

References

1. Williams, C.G., Phil. Trans., 150, 241, 1860

2. Staudinger, H., Fritschi, J., Helv. Chim. Acta, 5, 785, 1922

3. Staudinger, H., Geiger, E., Helv. Chim. Acta, 9, 549, 1926

4. Midgley, T., Jr., Henne, A.L., J. Am. Chem. Soc., 51, 1215, 1929

5. Bassett, H.L., Williams, H.G., J. Chem. Soc., 2324, 1932

6. Madorsky, S.L., Straus, S., J. Res. NBS, 53, 361, 1954

7. Brauer, G.M., J. Polymer Sci., Part C, 3, 1965

8. Wall, L.A., Straus, S., J. of Polymer Sci., 44, 313, 1960

9. Kolb, B., Kaiser, K.H., J. Gas Chromatog., 2, 233, 1964

10. Deur-Siftar, D., J. Gas Chromatog., 72, Feb., 1967

11. Oakes, W.G., Richards,R.B., J. Chem. Soc., 2929, 1949

12. Bulletin, Accessory for Gas Chromatograph GC 202, Bodensee Perkin-Elmer and Co., G.m.b.H., Germany

13. Groten, B., Anal. Chem., 36, 1206, 1964

14. Voigt, J., Kunststoffe, 54, 2, 1964

15. Barlow, A., Lehrle, R.S., Robb, J.C., Polymer, 2, 27, 1961

16. Strassburgh, J., Brauer, G.M., Tryon, M., Forziati, A.F., Anal. Chem., 32, 454, 1960

17. Bombaugh,K.J., Cook, C.E., Clampitt, B.H., Anal. Chem., 35, 1834,1963

18. Esposito, G.G., Anal, Chem., 36, 2183, 1964

19. Bailey, W.J., Liotta, C., Polymer Preprints, 5, 333, 1964

20. Bailey, W.J., Proc. Symp. Polypropylene Fibers, Birmingham, Alabama, 121, 1964

21. Moiseev, V.D., Neiman, M.B., Kriukova, A.I., Vysokomolekul. Soedin., 1, 1552, 1959

22. Tsuchiya, Y., Sumi, K., J. Polymer Sci., A-1, 7, 1599, 1969

23. Audisio, G., Bajo, G., Die Makromol. Chemie, 176, 991, 1975

24. Schooten, J. Van, Evenhuis, J.K., Polymer, 6, 343, 1965

25. Jernejcic, M., Premru, L., Rubber Chem. Technol., 41, 411, 1968

26. Galin-Vacherot, M., European Polymer J., 7, 1455, 1970

27. Van De Weil, H. J., Tommassen, P., J. of Chromato., 71, 9, 1972

28. Vacherot, M., Marchal, J., Rubber Chem. Technol., 41, 418, 1968

29. Binder, J.L., Ransaw, H.L., Anal. Chem., 29, 503, 1957

30. Hackathorn, M.J., Brock, M.J., J. Polymer Sci., Part B, 8,617, 1970

31. Galin, M.J., Macromol. Sci., Chem, A7, 873, 1973

32. Noffz, D., Benz, W., Pfab, W., J. Anal. Chem., 235, 121, 1968

33. Wolley, W.D., British Polymer J., 3, 186, 1971

34. O'Mara, M.M., J. Polymer Sci., A-1, 8, 1887, 1970

35. Iglauer, N., Bentley, F.F., J. of Chromato. Sci., 12, 23, 1974

36. Luce, C.C., Humphrey, E.F., Guild, L.V., Norrish, H.H., Coull, J., Castor, W.W., Anal. Chem., 36, 482, 1964

37. Barlow, A., Lehrle, R.S., Robb, J.C., Makromol. Chem., 54, 230, 1962

CHAPTER III

EXPERIMENTAL TECHNIQUES OF POLYMER PYROLYSIS-EVOLVED GAS ANALYSIS

Introduction

This Chapter is devoted to the discussion of the past and present techniques of polymer pyrolysis and evolved gas analysis. Representative literatures in this subject can be divided into three eras.

1. The pyrolysis pre-gas chromatographic era before early 1950's,
2. The pyrolysis-gas chromatographic era in the late 1960's, and
3. The present era of pyrolysis-gas chromatographic(PGC) on-line identifications.

Techniques of Polymer Pyrolysis-Evolved Gas Analysis

In 1949, Madorsky et al.[1] separated the pyrolyzates of synthetic polymers by pyrolytic fractionation in a specially designed apparatus. The sample was spread as a thin film on a platinum tray in a high vacuum at 300°-500°C. The products of pyrolysis were divided into a solid residue; a wax like fraction volatile at the temperature of pyrolysis but not at room temperature; a liquid fraction volatile at room temperature and; a gaseous fraction volatile at liquid nitrogen temperature. The liquid and gaseous fractions were analyzed with mass spectrometry(MS) which mass range was limited to about 105. The wax like fraction was tested for its average molecular weight(MW) by microfreezing point lowering method.

Some attempts were made to apply the latter method to the determination of the average MW of the solid residue but the temperature drop

was so insignificant that the results were totally unreliable. At that time, MS was a relatively new analytical technique and it required preliminary investigations of mass spectra of all individual pure compounds in a mixture before it could be used with due calibration to analyze sample mixtures. This imposed definite limitations and especially when the mass range was so limited.

It was not until 1952 when James and Martin[2] introduced gas chromatography(GC) that the problem of pyrolysis-evolved gas analysis could be better dealt with. The sensitivity, speed, accuracy and simplicity of this method offered a rapid means of volatile products analysis which otherwise, had to be done by more tedious separation methods. The major requirement of application of GC to chemical analysis is that the sample be a gas or liquid with sufficiently high vapor pressure. This fits well with polymer pyrolysis-evolved gas analysis.

When a pyrolysis unit is directly connected to the inlet of a GC, a number of requirements must be met for the successful separation of the pyrolysis products. Parameters such as the duration of pyrolysis, the nature of the carrier gas, and the flow rate through the unit, the pressure, the quantity of material, and the volume of the chamber are limited within the permissible values for optimum GC separation. Plug introduction of sample into the carrier gas stream is essential for good GC resolution. In general, two procedures are being used for introducing samples into the carrier stream of the GC. The first procedure involves condensing pyrolytic products in a cold trap and then by rapidly heating the trap, the products can be introduced as a plug to the inlet of the GC.

The second procedure employs pyrolyzing a minute quantity of the sample on a filament which is itself fitted into the inlet stream of the GC.

The filament is heated by electric current.

Perry[3] reported a typical filament pyrolyzer used in the 1960's. It consisted of some form of metallic elements on which the sample could be mounted and through which an electric current was passed. Most often, the metallic element consisted of a platinum or nichrome spiral.

This type of filament pyrolyzer had several disadvantages. In some cases, the sample was coated onto the filament by depositing from a suitable solvent and it was difficult to determine exactly how much sample was pyrolyzed. On the other hand, solvent might also contribute to the cracking pattern observed. In other cases, solid sample was placed on a particular turn of the filament helix and hence a considerable temperature gradient existed within the sample. This led to irreproducible cracking patterns.

Another disadvantage was the limited useful life-time of the filaments. The effect of carbon deposit on filaments after pyrolysis made it impossible to maintain constancy of temperatures unless coil currents were adjusted accordingly. In addition, the measurement of pyrolysis temperature had posed some difficulties and even if attempted, it was primarily based on optical pyrometry.

Even with PGC, positive identification of pyrolyzates at that time remained a problem although some post-GC analytical procedures had been used. PGC-MS was used but was not satisfactory because of the inherited disadvantages of MS. PGC-Polarography[4] with a specially constructed cell had been reported. This method was especially useful for polymers yielding electroreducible compounds. Major break through of pyrolysis-evolved gas analysis occurred in the late 1960's with the advent of a host of new analytical instruments, especilly those for post-GC on-line identifications.

Pyrolyzers were no longer individually designed by different workers in the field but were commercially available. This often meant better design and more reproducible results.

The first post-GC identification technique was vapor phase pyrolysis. The first report of this kind appeared in 1968 when Walker and Wolf[5] used this method to identify hydrocarbons. In general, the effluents from a GC were introduced by interrupted elution into a high temperature pyrolysis unit in which compounds were individually decomposed into simple molecules and separated again by another GC. The presence and to some extent the magnitude of some components such as CO, CH_4, CO_2, C_2H_4, C_2H_6, H_2S, NH_3, H_2O, and C_3H_6, offered functional group analysis. Whether a compound was a hydrocarbon, an acid, an ester, an aldehyde, a ketone, an alcohol, or a mercaptan could be determined[6].

Merritt and DiPietro[7] had reported a working graph of retention volume versus carbon numbers for different types of compounds. A complete bibliography of vapor phase thermal fragmentation was published by Sarner[8]. On-line elemental analysis of GC effuents for the determination of respective empirical formulae was reported by Liebman and co-workers[9].

More recent post-GC on-line identification technique involves rapid scan vapor phase infrared(IR) spectrophotometry[10]. This method is not without its limitation. For pure compounds, the detailed structure of an IR spectrum almost invariably permits unique, fingerprint identification of a compound when a matching reference spectrum can be found. However, IR will not be very helpful for members of a homologous series, e.g., for hydrocarbons with various chain length and/or substituted alkanes. The most recent development in post-GC identification is the combination of IR and nuclear magnetic resonance(NMR)[11]. NMR complements the IR and is able to provide the additional information for identification.

Interfaced Pyrolysis Gas Chromatographic Peak Identification System (IPGCS)

Thermal decomposition of polymers is a very complicated process. In pyrolysis experiments, small samples are decomposed into many products which have to be collected for analysis. One usually finds serious discrepancies in the literature with regard to the results of thermal decomposition of polymers, particularly those pertaining to rates and activation energies. These discrepancies are probably due to differences in apparatus, procedures, method of measuring temperatures and loss of weight of samples, as well as to differences in the methods of analysis of the results by different workers. Therefore, in order to compare results, it is essential to know the configuration of the apparatus and the experimental procedures employed by other workers.

The following is a brief description of the versatile IPGCS used in this study[12]. It incorporates instrumentation for thermal decomposition under slow and ultra-rapid temperature rise conditions. Evolved volatiles are transferred to a master trap manifold where precolumn procedures may be applied prior to GC separation. Identification of each individual peak is then performed on-the-fly by rapid scan vapor phase IR spectrophotometry; elemental analysis for carbon, hydrogen, oxygen, nitrogen, etc.; functional group fingerprinting by vapor phase pyrolysis; and molecular weight determination by differential gas density measurement(Mass Chromatography). An interfaced laboratory computer is available for data acquisition, reduction and control. A block diagram of the IPGCS is shown in Figure 1. In order to make clear the operation of the system, a brief discussion of each individual instrument follows.

The MP3 multi-purpose thermal analyzer is manufactured by the Spex

Industries. It pyrolyzes sample at programmed rates from 4° min^{-1} to 40° min^{-1} up to 1000°C. It was modified by the addition of two laminar flow controllers (HGC 187; Analab) which provide controlled atmospheres of up to three gaseous mixtures. The CDS 820 (Chemical Data Systems) consists of a Pyroprobe 100 capable of delivering to a polymer sample a maximum heating rate of 20,000° sec^{-1}; the CDS 820 provides a controlled atmosphere for the Pyroprobe.

The master GC is a Varian 2760 instrument with thermal conductivity and flame ionization detectors. A second Varian 2760 GC-2 serves for analysis of samples from two sources, pyrolysis products from the CDS 820, and from the structural determination function of the CDS 1200. The latter instrument (Chemical Data Systems) is a functional group and elemental analyzer which generates a vapor phase thermolytic fragmentation pattern for functional group analysis and also performs elemental analysis. The effluent from the master GC is split so that 10 percent of it is directed to the detector and 90 percent of it to the CDS 1200. A stop-flow valve admits one peak at a time thus enabling the analysis of all the components of the pyrolysates without appreciable peak spreading. The use of CDS 1200 in organic analysis has been discussed by Liebman et al.[9].

The Norcon 201 rapid scan vapor phase IR spectrophotometer is a double beam grating instrument which scans a spectrum from 4000 to 670 cm^{-1} in either 6 seconds or 30 seconds, with recycle times of 8 and 40 seconds, respectively. Its wavelength accuracy is $\pm$ 0.05μ with $\pm$ 0.025μ reproducibility. The sample cell has a volume of 5 ml and is constructed of gold coated glass (4 x 4 mm cross section, 30 cm in length). The path length to volume ratio is 6.0 cm^{-2}. The cell is enclosed in an oven regulated to $\pm$ 2.5° from 120° to 250°C. The Norcon 201 is connected to the master GC through heated transfer line. Effluent fraction of 0.025 λ is sufficient to yield a good

spectrum. The Norcon 201 is interfaced with a PDP 11/10E computer system. This system has a RT 11 foreground/background operating soft ware, FORTRAN, and Lab Applications Program Library V03 which contains SPARTA and THRU programs for data acquisition and a IRFLAV program for the acquisition of IR spectral data with digital filtering. Another routine, IRSPBA, performs background subtraction, and spectrum print out.

The MC-2 mass chromatograph (Spex Industries) determines molecular weight of GC eluent through differential gas density mearsurements. A sample is split into two equal fractions; they are carried by two different gases, CO_2 and Freon 115, through two matched GC columns into density balance detectors. The molecular weight of the unknown is obtained from

$$MW = \frac{(A_1/A_2)\ K\ MW_{CG1} - MW_{CG2}}{(A_1/A_2)K - 1} \tag{1}$$

where the instrument constant K is calibrated with a substance of known molecular weight, MW_{st},

$$K = \left(\frac{A_1}{A_2}\right)\left(\frac{MW_{st} - MW_{CG1}}{MW_{st} - MW_{CG2}}\right) \tag{2}$$

In these equations MW_{CG1} and MW_{CG2} are the molecular weights of the two carrier gases, and A_1/A_2 is the ratio of peak height response of a standard for the detectors.

The accuracy for the determination of molecular weight with MC-2 depends upon the instrument constant K (Equation 2). The best results are obtained for values of K determined with known compounds having molecular weights nearly the same as the unknown. Lloyd et al.[13] had developed a least square curve fitting program to fit the calibration K values to a

polynomial which was then used in an iterative procedure to calculate the molecular weights of the unknown. The molecular weights thus obtained are accurate to $\pm$ 1 mass unit as judged by comparison with mass spectrometric results. The advantages of the simple MC-2 mass chromatography are offset by the loss of information about geometric isomerism. Therefore, the technique must be used together with mass spectrometry.

In addition to the above IPGCS system, other thermoanalytical techniques were also employed in this work. This includes a conventional pyrolysis-GC-MS system which consists of a CDS Pyroprobe 100, a Perkin-Elmer 990 GC, and a Hitachi-Perkin-Elmer RMU 6L MS, as well as a DuPont 900 thermal analyzer.

The CDS Pyroprobe 100 is based on a precision platinum element that serves as a temperature sensor, heater and sample holder simultaneously. This element forms one leg of a conventional Wheatstone bridge circuit and the temperature setting control forms a balancing leg. By electronically programming the balancing leg, very rapid linear heating rates are obtained.

The DuPont 900 thermal analyzer is the basic console of the DuPont modular thermal analysis system. A variety of modules and accessories plug into the 900 thermal analyzer. These include modules for differential thermal analysis(DTA), differential scanning calorimetry(DSC), thermogravimetric analysis(TGA), and thermomechanical analysis(TMA).

Experimental Procedures

Typical pyrolysis – evolved gas analysis experiments in this study are described as follow.

To get a pyrogram with the IPGCS, the instruments involved were the combination of the MP3, the master trap manifold, and the master GC. Weighed polymer sample was placed into the quartz tube at the inlet of the MP3. The tube itself was positioned between the two halves of the MP3 oven and was constantly purged with a gas; depending on whether it was pure pyrolysis or oxidative pyrolysis; at 25 ml min^{-1}. Meanwhile, the glass bead trap on the master trap manifold was rapidly heated to about 300°C and whatever residual substances in it were vented. A blank chromatogram was then obtained with the separation column in the master GC to ensure that no alien compound remained in the column. The master GC was then cooled and ready for experiment.

The MP3 oven was first heated to some final temperatures as determined by a previous TGA on the same polymer. When the oven had attained its final temperature, it was then moved towards the portion of the quartz tube which contained the sample. About 30 seconds were required for the oven to equilibrate to its final temperature. The sample was held at some pre-determined periods of pyrolysis time. A fan was used to cool the oven rapidly after each pyrolysis.

The pyrolytic products, carried along by the carrier gas, passed through heated transfer line to the master trap manifold where they were collected in the glass bead trap at liquid nitrogen temperature. The trap was then heated rapidly and products were backflushed into the separation column in the master GC. The pyrogram was obtained with a flame ionization detector and/or a thermal conductivity detector.

For post-GC on-line identification involving rapid scan vapor phase IR, the delay time; at fixed GC carrier gas flow rate, IR oven temperature, and heated transfer line temperature; was determined. The delay time

allowed the sample to pass through the heated line from the master GC detector to the IR sample cell. Acetone was used for this purpose and it was injected through the master GC to the IR spectrophotometer. The delay time was then obtained by a calibration chart provided by the manufacturer.

A reference pyrogram was first obtained so as to decide which peaks were to be sampled. The select valve on the master trap manifold was then turned to IR for sampling. Another pyrogram was obtained under similar conditions and when a peak of interest was eluting, a remote control switch was activated and the IR spectrum was taken after the pre-set delay time. IR data acquisition, background substraction, and spectra print out were performed by the PDP 11/10E computer.

For post-GC identification involving vapor phase pyrolysis, a reference pyrogram was again obtained by the master GC. The select valve on the master trap manifold was turned to the CDS 1200 for sampling. An identical pyrogram was then obtained and peaks of interest were introduced into the instrument by interrupted elution. Vapor phase pyrolysis was performed at 800°C by non-catalytic thermal dissociation in a gold reactor. Eight minutes were required for a complete dissociation reaction. Pyrogram for each compound was then obtained by GC2.

For post-GC identification involving molecular weight determinations by the MC2 Mass Chromatograph, the latter instrument was first calibrated by n-alkanes injected directly into the instrument. Pyrolyzates were transferred directly from the MP3 to the trap on the MC2 instrument. The trap was then heated rapidly and the products were backflushed into the dual columns for separation. Gas density balance detectors were used and the molecular weight of each product was determined from its respective peak heights by the least square curve fitting program developed by Lloyd et al.[13].

For post-GC identification involving MS, a combination of MP3, Perkin-Elmer 990 GC, and Hitachi-Perkin-Elmer RMU 6L MS was used. Of these three instruments, only the MP3 belongs to the IPGCS. The sample was pyrolyzed on the MP3 and products were collected in the glass bead trap in liquid nitrogen at the master trap manifold. The glass bead trap, while still in liquid nitrogen, was detached from the manifold and hooked onto the inlet portion of the Perkin-Elmer 990 GC. The trap was wound with heating wire and was able to heat up very rapidly to 250°C by Powerstat. The setting on the Powerstat and the heating duration were pre-determined by a thermocouple. The trap was then heated and products were sent into the GC. A reference pyrogram was first obtained. This was followed by an identical run where as a peak of interest was emerging, the splitter valve to the MS was opened to admit the sample.

Finally, the rates of decomposition of the polymer were obtained by weighing the residue after each pyrolysis at different temperatures and for different periods of pyrolysis time. The activation energy for the pyrolysis process was determined from the Arrhenius equation.

$$K = A \exp\left(-\frac{E}{RT}\right)$$

where
- K = rate constant
- A = frequency factor
- R = gas constant
- T = absolute temperature
- E = activation energy

Conclusion

The techniques of pyrolysis-evolved gas analysis have indeed come a long way to the present status through better instrumentation. In the pre-GC era, pyrolytic fractionation was the only method of separating pyrolysis products. Product identifications were carried out either by primitive MS or by microfreezing point method. The introduction of GC greatly facilitated the separation process, however, post-GC identification of evolved gases still remained a problem. Although a good separation method, GC is a poor qualitative and quantitative tool which requires extensive calibrations.

Recent post-GC identification techniques employ vapor phase pyrolysis, elemental analysis, rapid scan vapor phase IR and/or NMR, and MS have definitely enhanced the study of evolved gases. This is important in understanding the mechanisms of flame retardation of polymers and in qualifying products to meet flammability standards.

References

1. Madorsky, S.L., Straus, S., Thompson, D., Williamson, L., J. of Res. NBS, 42, 499, 1949
2. James, A.T., Martin, A.J.P., Analyst, 77, 915, 1952
3. Perry, S.G., J. of Gas Chromato., 54, 1964
4. Maivanovki, V.G., Yanotovski, M.T., Zh. Fiz. Khim, 37, 705, 1963
5. Walker, J.Q., Wolf, C.J., Anal. Chem., 40, 711, 1968
6. Groenendyk, H., Levy, E., Sarner, S.F., J. of Chromato.Sci., 8, 599, 1970
7. Merritt, C., JR., DiPietro, C., Anal. Chem., 44, 57, 1972
8. Sarner, S.F., J. of Chromato. Sci.,10, 65, 1972
9. Liebman, S.A., Ahlstrom, D.H., Nauman, C.D., Averitt, R., Walker, J.L., Levy, E.J., Anal. Chem., 45, 1360, 1973
10. Penzias, G.J., Anal. Chem., 45, 890, 1973
11. Shaps, R.H., Simons, W., Varano, A., American Lab., 95, March, 1977
12. Uden, P.C., Henderson, D.E., Lloyd, R.J., J. of Chromato., 126, 225, 1976
13. Lloyd, R.J., Henderson, D.E., Uden, P.C., Anal. Chem., 48, 1645, 1976

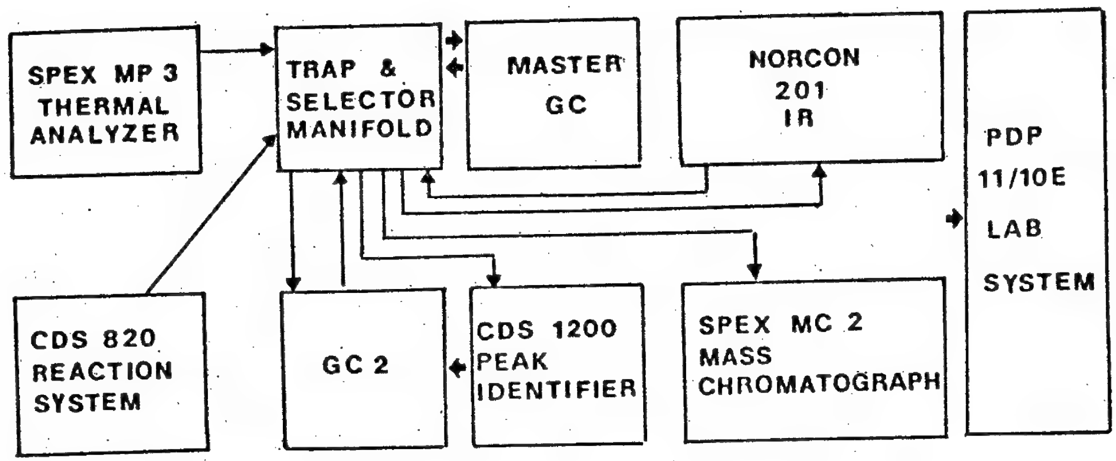


Fig. 1 Block diagram of interfaced pyrolysis gas chromatographic peak identification system

CHAPTER IV

PYROLYSIS OF POLYPROPYLENE

Abstract

Amorphous and semi-crystalline polypropylene(APP and IPP) were pyrolyzed in helium from 388°-438°C with a novel interfaced pyrolysis gas chromatographic peak identification system(IPGCS). The products were identified on-the-fly by mass chromatography and mass spectrometry. The products were mostly olefins and a simple mechanism was proposed which involved intramolecular chain transfer processes of the primary and secondary alkyl radicals, the latter radicals being of greater importance.

The pyrolysis of polypropylene in inert atmosphere followed first-order reaction kinetics and activation energies of 51-56 Kcal $mole^{-1}$ were determined for the two polypropylene samples.

Introduction

When various polymers were burned in air in a 'candle-like' manner[1], the maximum flame temperatures were 490°-740°C and the temperatures of the melt surface 230°-540°C. Burge and Tipper[2] found the temperature of polyethylene to be 400°-500°C at the burning surface decreasing to 200°-300°C at 1 cm below the surface. Whether the temperature being greater when the decomposition processes for the polymers are pure pyrolysis or oxidative pyrolysis is still largely unsettled.

It had been shown that the oxygen concentration 1 mm above the surface of a burning polyethylene rod was only about 1 percent[2]. Similar results were reported for polypropylene[3]. From this it may be inferred that the

polymer in the melt surface may be oxygen depleted. On the other hand, the polymer further below the surface probably contains the usual amount of dissolved oxygen. It is likely that oxidative pyrolysis contributes significantly or even predominately to the liberation of volatile and combustible fragments from the polymer. The relative importance of pure pyrolysis and oxidative pyrolysis can only be established by experimentation. This study deals with the pure thermal decomposition of polypropylene. The results on APP and IPP are presented and compared with reported studies. The IPGCS and the flash pyrolysis-GC-MS system used for experimentation were described in Chapter III.

Experimental

The APP used was the unstabilized Eastobond M-5W(x12815-14-1) from Tennessee Eastman. The polymer was washed with benzene, precipitated with acetone and vacuum dried for 2 days. The semi-crystalline polypropylene was Profax 6501, unstabilized IPP from Hercules Incorporated. It has a crystallinity of 61 percent as determined from its density[4]; a weight-average molecular weight of about 24,000; a molecular weight distribution of 11; and an ash content of about 0.01 percent[5]. The polymer was used without purification.

In the flash pyrolysis-GC-MS experiment, about 1 mg of IPP was weighed into a quartz tube which was inserted into the heating coil of the CDS Proprobe 100. The latter was fitted directly into the injection port of the Perkin-Elmer 990 GC. The GC was operated at a manifold temperature of 220°C; injector temperature of 210°C; GC-MS interface temperature of 255°C; He carrier gas flow rate of 83 ml min^{-1}; and with a flame ionization detector. Samples were pyrolyzed at 600°, 650°, 700°, 750°, 800°, 850°,

900°and 950°C at a heating rate of 20,000°C sec^{-1}. All samples were pyrolyzed for 20 seconds at these final temperatures.

Two columns were used to separate the pyrolysis products with temperature programming from 1° min^{-1} to 6°C min^{-1}. A Porapak Q column (4 ft x 1/8" O.D.) was used to separate the low-boiling compounds and a 4 percent SE 30 on ABS column (6 ft x 1/8" O.D.) was employed for higher boiling products. This was followed by identical runs where as a peak of interest was just emerging, the interface splitter valve was opened to admit the sample into the MS. The latter was operated at an electron energy of 70 eV and a filament current of 3.4 amphere.

Thermogravimetric analysis(TGA) for APP and IPP at a helium flow rate of 25 ml min^{-1} and a heating rate of 30°C min^{-1} was performed with the DuPont 900 thermal analyzer. These experiments provided the choice of temperatures of pyrolysis for conveniently measureable rates.

All pyrolyses with the IPGCS were performed with the MP3 multipurpose thermal analyzer. The instrument was operated with a casting temperature of 225°C and a transfer line (from the MP3 to the master trap manifold) temperature of 300°C. The oven was first calibrated with a Hewlett-Packard digital voltmeter 3439A. The calibration was performed by inserting an iron-constantan thermocouple through the rubber septum into the quartz tube sample holder. The latter was purged with helium carrier gas at 25 ml min^{-1} as if in actual pyrolysis experiment. A temperature calibration curve was thus constructed.

About 2 mg of polymer was weighed into the quartz tube of the MP3 and was purged with helium for 4 minutes so as to get rid of residual air in the system. The polymer was then pyrolyzed at 388°, 414° and 438°C at a heating rate of 40°C min^{-1} and with a helium carrier gas flow of 25 ml

min^{-1}. The products, after passing through the master trap manifold, were collected in a 1 ft x 1/8" O.D. glass bead column in liquid nitrogen. The master trap manifold was operated at about 280°C. After all of the products had been collected, the glass bead trap was heated rapidly to 300°C and the products were backflushed into the master GC for separation. The transfer line from the master trap manifold to the master GC, and the inlet portion of the GC column were all operated at about 300°C.

The low and high-boiling hydrocarbons were separated respectively with a Chromosorb 102 column(12 ft x 1/8"O.D.) and an 8 percent Dexsil 300 GC on Chromosorb WHP column(6 ft x 1/8" O.D.). The pyrograms were obtained with a flame ionization detector. At a helium carrier gas flow rate of 14 ml min^{-1}, the columns were first kept isothermally at 37°C for 3 minutes, then programmed at 4°C min^{-1} to a final temperature of 250°C for the Chromosorb column and to 300°C for the Dexsil column. The molecular weights of the products were determined with the MC2 Mass Chromatograph which was pre-calibrated with n-alkanes. The relative weight percentage of the products were calculated from the intergrated areas of the GC peaks taking into considerations the attenuation factors. Dietz[6] had shown that the flame ionization detector is equally sensitive to almost all hydrocarbons.

For kinetic studies, the MP3 oven was first heated up to 388°C and then moved rapidly over to the sample which was at room temperature. Thirty seconds were required for the oven to return to its original temperature. Since the sample tubing was only 5 mm in O.D., it was assumed that the sample also attained 388°C in 30 seconds. The oven was cooled with a fan after each pyrolysis and the weight of the residue was obtained with a microbalance. The experiments were repeated at 414° and 438°C respectively and for different periods of pyrolysis time.

Results

Figure 1 shows the TGA curves in helium for APP and IPP respectively. Figure 2 compares their corresponding percent weight loss versus temperatures. From this figure, the temperature for 50 percent weight loss of each sample can be obtained. The results of the rates of pyrolysis for the two samples are shown in Figure 3. The pyrolysis processes followed first-order reaction kinetics as shown in Figure 4 which is a semilog plot of the weight of polymer residue versus pyrolysis times. The activation energies were determined from Arrhenius plots as shown in Figure 5. The rate constants at different temperatures and the activation energies for the pyrolysis of APP and IPP are summarized in Table 1.

Table 1

Kinetics of the Pyrolysis of APP and IPP in Helium

	Rate Constants, sec^{-1}	
Temp, °C	APP	IPP
388	3.7×10^{-4}	4.0×10^{-4}
414	1.4×10^{-3}	1.1×10^{-3}
438	7.6×10^{-3}	6.2×10^{-3}
Activation Energy, Kcal $mole^{-1}$	56	51

By comparison, IPP decomposed faster than APP at 388°C but more slowly at 438°C. This was reflected by a lower activation energy of 51 Kcal $mole^{-1}$ for IPP. The accuracy for the activation energy is about 10 percent. The lower activation energy of IPP is probably due to the catalytic effect of the ash that remained in the polymer after polymerization.

Tomita[7] had shown that the thermal degradation of poly(ethylene terephthalate) was accelerated by residual metal catalysts.

The pyrograms of IPP at 438°C are shown in Figures 6 and 7. The numbers adjacent to each peak represent the detector attenuation factors. The products and their distributions are shown in Tables 2, 3, and 4. In Table 2, the molecular weights were determined by mass chromatography. The first three peaks of the MC2 pyrogram were thwarted by the instability of the base line during the first few minutes of operation. These compounds were identified by retention times of authentic compounds and verified by vapor phase pyrolysis with the CDS 1200 instrument. The chemical structures of these products were obtained by MS.

Table 3 shows the relative weight percentage of each product basing on total volatiles up to C_{13}. Table 4 shows the product distributions of the pyrolysis of APP and IPP at 388° and 414°C, pyrolyzed for 60 minutes and 3 minutes respectively. Table 5 presents the fragmentation patterns of the major flash pyrolysis products of IPP from 600° to 950°C.

Similar products were obtained by the slow and flash pyrolysis (Tables 2 and 5) despite the huge difference in temperatures. The rates of product formations at 414°C are shown in Figures 8 and 9. These figures are normalized for each product and show the fraction of the product obtained as a function of time.

Table 2

Pyrolysis Products of Poly(propylene) at 438°C

Peak	Molecular Weight[b]	Hydrocarbons[c]
1[a]		CH_4 (methane)
2[a]		C_2H_6 (ethane)
3[a]		C_3H_8 (propylene)
4	55.7	C_4H_8 (isobutylene)
5	70.0	C_5H_{10} (2-pentene)
6	81.2	C_6H_{12} (3-methyl-1-pentene)
7	96.8	C_7H_{12} (3-methyl-3,5-hexadiene)
8	110.0	C_8H_{16} (4-methyl-3-heptene)
9	123.5	C_9H_{16} (2,4-dimethyl-heptadiene)
10	125.9	C_9H_{18} (2,4-dimethyl-heptene)
11	139.5	$C_{10}H_{20}$
12	157.5	$C_{11}H_{22}$ (4,6-dimethyl-3-nonene)
13	168.2	$C_{12}H_{24}$ (2,4,6-trimethyl-8-nonene)
14	180.6	$C_{13}H_{24}$

[a]Identified by retention time and vapor phase pyrolysis

[b]Molecular weight determined by mass chromatography

[c]Structure determined by mass spectrometry

Table 3

Relative Weight Percentage of Pyrolytic Products of IPP and APP at 438°C[a]

	Pyrolysis Time, min					
	IPP			APP		
Products	1	2	4	1	2	4
CH_4	0.08	0.08	0.1	0.1	0.08	0.13
C_2H_6	1.3	1.2	1.0	1.2	1.0	1.3
C_3H_6	9.7	11.0	10.0	13.0	11.0	16.0
C_4H_8	2.0	2.6	2.5	3.1	2.9	3.5
C_5H_{10}	15.0	15.0	14.0	16.0	14.0	16.0
C_6H_{12}	9.4	10.0	9.4	11.0	11.0	12.0
C_7H_{12}	1.4	1.8	1.6	1.9	1.8	1.6
C_9H_{18}	41.0	40.0	40.0	35.0	40.0	34.0
$C_{10}H_{20}$	2.2	1.8	2.1	2.2	2.2	2.2
$C_{11}H_{22}$	1.5	1.5	1.5	1.3	1.2	1.5
$C_{12}H_{24}$	10.0	9.4	9.7	9.4	8.7	9.0
$C_{13}H_{24}$	1.6	1.6	1.8	1.6	1.6	1.7
unidentified	4.7	3.8	6.7	4.7	5.1	3.5

[a]Obtained by MP3 pyrogram

Table 4

Pyrolysis Products of Poly(propylene) at 388° and 414°C[a]

Hydrocarbons	Pyrolysis Temperature, °C 388 wt. % of products APP	IPP	414 wt. % of products APP	IPP
CH_4	0.09	0.08	0.08	0.12
C_2H_6	0.9	0.7	1.0	1.6
C_3H_6	9.0	7.0	11.0	12.0
C_4H_8	2.7	1.8	2.7	2.1
C_5H_{10}	15.0	14.0	17.0	19.0
C_6H_{12}	12.0	11.0	10.0	12.0
C_7H_{12}	1.1	1.0	1.6	1.4
C_9H_{18}	43.0	45.0	41.0	36.0
$C_{10}H_{20}$	1.7	1.5	2.2	1.5
$C_{11}H_{22}$	2.4	3.1	1.7	2.0
$C_{12}H_{24}$	11.0	14.0	11.0	12.0
$C_{13}H_{24}$	1.4	1.6	1.3	1.2

[a]Obtained by MP3 pyrogram

Table 5

Identification of Pyrolysis Products of Poly(propylene) by Mass Spectrometry

Product	Fragmentation Patterns in Mass Numbers
Methane	16, 15
Ethylene	28, 27, 26
Propylene	42, 41, 27
Isobutane	58, 43
2-Pentene	70, 55, 42, 41, 39
3-Methyl-1-pentene	84, 69, 56, 41
3-Methyl-3,5-hexadiene	96, 81, 67, 55, 41, 39
4-Methyl-3-heptene	112, 69, 55, 41, 39, 27
2,4-Dimethyl-heptadiene	124, 123, 109, 95, 82, 67, 55, 41, 39
4,6-Dimethyl-3-nonene	154, 111, 85, 69, 55, 43, 41, 39
2,4,6-Trimethyl-8-nonene	168, 153, 125, 111, 97, 83, 69, 57, 43
2,4,6,8,10-Pentamethyl-3,9-undecadiene	222, 207, 179, 166, 151, 137, 123, 109, 95, 83, 69, 55, 41
2,4,6,8,10-Pentamethyl-1-undecene	224, 210, 168, 153, 141, 125, 111, 97, 83, 69, 57, 43

Discussion of Results

There have been quite a few published studies of pyrolysis of polypropylene. They are more in discord than in agreement. Different kinetics, activation energies and products were reported due to variations in experimental conditions, procedures, apparatus and sample size used.

Wall and Straus[8] found the rate of volatilization of polypropylene at 375°C to increase rapidly to a maximum at 40 percent conversion then decreased rapidly with further heating. Similar behaviors were also observed for polyethylene[8], however, branches longer than a methyl group were found to eliminate the maxima in the rate curves even when present in quite low concentration[9]. On the other hand, Madorsky and Straus[10], and this work found the kinetics of pyrolysis to be first-order.

Even though the pyrolysis of polypropylene is mechanistically complicated, the kinetics are first-order because the rate determining step is the homolysis of the C-C bond describable by a well defined rate constant. In this study, the activation energies for the pyrolysis of IPP and APP were 51 and 56 Kcal mole^{-1} respectively. Other literature values were 59 Kcal mole^{-1} measured at 380°-400°C by Straus and Wall[11]; 58 Kcal mole^{-1} in the range 328°-410°C reported by Madorsky[12]; and 55 Kcal mole^{-1} found by Moiseev et al.[13] in the temperature range of 320°-420°C.

The difference in the activation energies for IPP in this study and others is probably due to the difference in molecular weight of the samples. Madorsky[14] in his text had tabulated the relationship of molecular weights versus activation energies for the thermal degradation of high density polyethylene. The activation energy decreased from 61 to 53 Kcal mole^{-1} for samples with molecular weight of 23,000 and 16,000 respectively. The

difference in activation energies can also be due to the difficulty associated with temperature measurements. Madorsky[11] had shown that these measurements depended on the relative positions of the sample and the thermocouple. In this study, pyrolysis temperatures depend on the precise calibration of the MP3 oven. The maintenance of an uniform temperature throughout the polymer sample due to its poor conductivity could also be a problem, especially when the decomposition reactions involved are endothermic.

The pyrolysis products in our work were found to be predominantly olefins. Small amount of methane was found at all temperatures. Minor quantities of ethane were observed at low temperatures and isobutane in flash pyropysis. The most significant difference between slow and flash pyrolysis at high temperatures was C_9 hydrocarbons. In slow pyrolysis, 2,4 dimethyl heptene was the major product and 2,4 dimethyl heptadiene was present only to a minor extent. However, in flash pyrolysis, only the latter product was observed. The formation of 2,4 dimethyl heptadiene is probably due to the secondary reaction of 2,4 dimethyl heptene. The absence of this latter product in flash pyrolysis could be either due to non-preferential fragmentation of flash pyrolysis or to the higher temperatures in this experiment.

The major products shown in Tables 2, 3 and 4 were peaks 3(propylene), 4(isobutylene), 5(2-pentene), 6(methyl pentene), and 10(dimethyl heptene). Significant amounts of 13(trimethyl nonene) were also identified. These results are most similar to those of Tsuchiya and Sumi[15] except for certain products. Their major product was also 2,4 dimethyl heptene. However, they found pentane as one of the major products, they also identified 4 methyl heptane. They did not identify pentene, 4 methyl heptene and 2,4 dimethyl

heptadiene which were found in this work. The discrepancy could be explained by different experimental conditions in the two studies. Tsuchiya and Sumi performed the experiment in vacuum whereas in this work pyrolysis was conducted in a constant sweeping atmosphere. The main products were found by Moiseev et al.[13] to be pyropylene, isobutylene and pentene. At the other end of the spectrum, Bailey and Liotta[16,17] found that at 340°C pyrolysis of polypropylene yielded 80-90 percent propane and 65 percent n-pentane at 380°C.

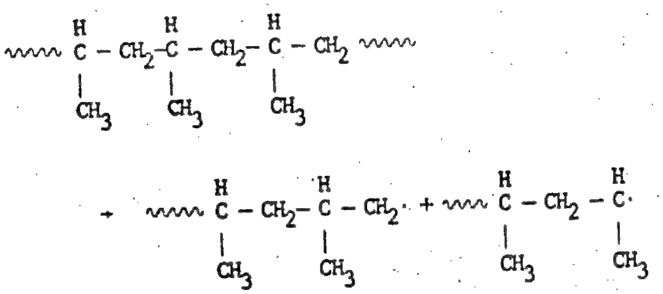
Madorsky[14] studied the pyrolysis products over the widest temperature range from 380°-1200°C. At the low temperature regions; propylene, isobutylene, butane, pentene, pentane, and hexene were the major products. However, the amount of pentane found was only 11 mole percent as compared to 65 and 31 percent reported by Bailey and Liotta[16], and Tsuchiya and Sumi[15] respectively. Madorsky[14] also observed that between 400°-800°C, the major products were produced in nearly the same amounts except for propylene, the yield of which increased suddenly suggesting unzipping of the polymer. Schooten and Evenhius[18] performed pyrolysis hydrogenation-GC study on polypropylene. The limitation imposed by combining olefins and paraffins precluded a more complete explanation of the mechanism.

Finally, APP and IPP seemed to be slightly different in their pyrolysis behavior as had also been noted by Bresler et al.[19]. This study had shown (Figure 2) that the temperatures for 50 percent decompisition of APP and IPP were 425°and 410°C respectively. However, the differences are not too great and their significance needs further verification.

In order to reconcile to some degree the above cited results, the mechanism for pyrolysis of polypropylene needs to be considered. The

mechanism commonly accepted is based on those proposed for the gas-phase degradation of simple hydrocarbons[20,21].

Chain Initiation



(1)

(I) (II)

In Equation 1, I is a primary aliphatic radical and II is a secondary radical. In highly stereoregular and pure polypropylene initiation is the result of thermal homolysis. However, most commercial polymers contain small percentages of impurities and structural irregularities. Chain initiation via scission of weak links cannot be ruled out as a possibility.

Unzipping (depolymerization)

$$\text{I or II} \rightarrow \text{I}' \text{ or II}' + CH_3\text{-}\overset{H}{C}{=}CH_2 \quad \text{(propylene)} \qquad (2)$$

For polymers with low ceiling temperature, such as poly(α-methylstyrene) and poly(methylmethacrylate), unzipping is the predominant degradative process. However, this is unimportant for pyrolysis of poly(propylene) at low temperature. Unzipping becomes more important above 800°C but still is not the dominant reaction.

Chain Transfer

(a) Intramolecular Chain Transfer Intramolecular hydrogen transfer[21] leads to many of the observed products. In the Equations below the numbers above the arrows indicate the modes of hydrogen transfer. Not all of the possible products were found in this study; the underlined products correspond to those found in significant amounts experimentally.

From the primary radical

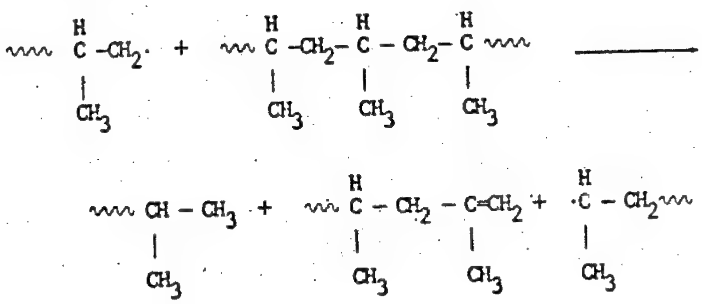
$$\begin{aligned}
\mathrm{I} \quad &\xrightarrow{\;1,2\;} \mathrm{II} + \underline{\text{isobutylene}} \\
&\xrightarrow{\;1,3\;} \mathrm{I} + \text{4-methyl-2-pentene} \\
&\xrightarrow{\;1,4\;} \mathrm{II} + \text{2,4-dimethylpentene} \\
&\xrightarrow{\;1,5\;} \mathrm{I} + \underline{\text{4,6-dimethyl-heptene}} \\
&\xrightarrow{\;1,6\;} \mathrm{II} + \text{2,4,6-trimethylheptene} \\
&\xrightarrow{\;1,7\;} \mathrm{I} + \underline{\text{4,6,8-trimethyl-nonene}} \\
&\xrightarrow{\;1,8\;} \mathrm{II} + \text{2,4,6,8-tetramethylnonene}
\end{aligned} \tag{3}$$

From the secondary radical

$$\begin{aligned}
\mathrm{II} \quad &\xrightarrow{\;1,2\;} \mathrm{I} + \underline{\text{2-pentene}} \\
&\xrightarrow{\;1,3\;} \mathrm{II} + \underline{\text{2-methylpentene}} \\
&\xrightarrow{\;1,4\;} \mathrm{I} + \underline{\text{4-methyl-heptene}} \\
&\xrightarrow{\;1,5\;} \mathrm{II} + \underline{\text{2,4-dimethylheptene}}
\end{aligned} \tag{4}$$

$$\text{II} \xrightarrow{1,6} \text{I} + \underline{\text{4,6-dimethyl-nonene}}$$
$$\xrightarrow{1,7} \text{II} + \underline{\text{2,4,6-trimethylnonene}} \qquad (4)$$

(b) Intermolecular Transfer

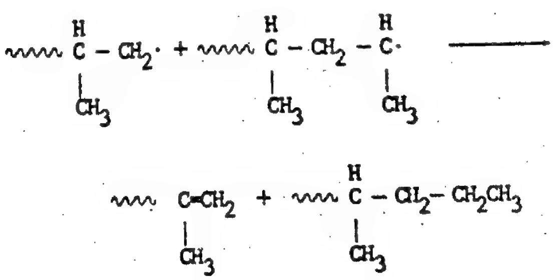


(5)

This process does not produce volatile products directly.

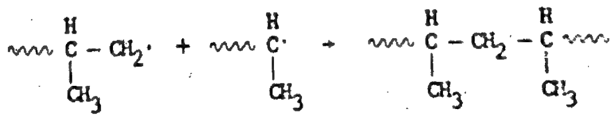
Chain Termination

Termination is thought to occur either by disproportionation of radicals,



(6)

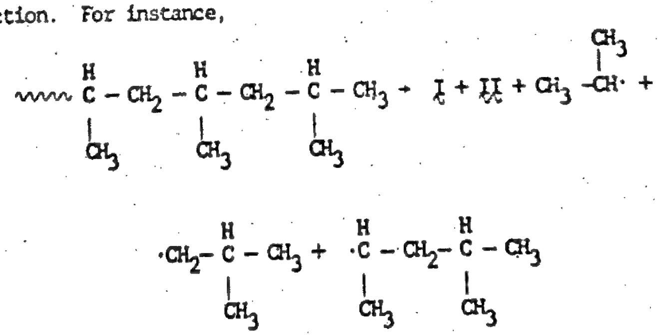
or others between I and II in different combinatory paths, or by combination of radicals.



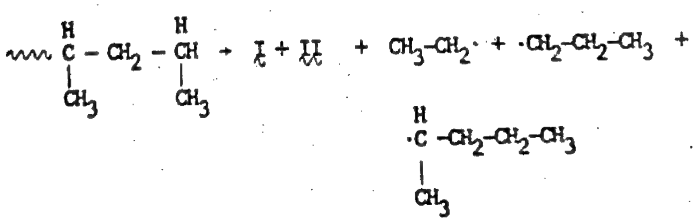
(7)

The results of this study are consistent with pyrolysis of poly(propylene) proceeding mainly by the intramolecular chain transfer involving the secondary alkyl radical. It accounts for the fact that most of the volatile products were olefins (Table 2) and that olefins from C_3 to C_{13} were all formed. Furthermore, C_9H_{18} was formed by 1,5 hydrogen transfers of both radicals I and II; this should make this the most abundant product and was, in fact, observed. Also, $C_{12}H_{24}$ was produced by 1,7 hydrogen transfers of both radicals I and II making it a significant pyrolysis product as well.

The obvious way saturated hydrocarbons such as propane, butane, and pentane could be formed in significant quantity would be if chain initiation was primarily from the polymer chain ends followed by hydrogen abstraction. For instance,



(8)



(9)

Termination involving these radicals could also lead to alkanes and some olefins as well. The reason why initiation at polymer chain ends dominates in some works is not clear, and may be enlightened by pyrolysis studies of poly(propylene) prepared by initiation with different alkyls such as $Al(Me)_3$, $Al(Et)_3$, or $Al(iBu)_3$.

One major difference between the experimental procedure in this work and those of others was that the pyrolysis products were swept away by the He carrier gas whereas most other studies were carried out in closed evacuated vessels. It would seem that secondary reactions were much less likely to occur under the former conditions although Madorsky[14] in his text had claimed the opposite. Dienes were secondary pyrolysis products, so were some of the alkanes.

Conclusion

A novel interfaced pyrolysis gas chromatographic peak identification system had been used to study the pyrolysis of polypropylene. The major pyrolytic products were olefins: propylene, isobutylene, pentene, methylpentene, dimethylheptene, and trimethylnonene. A mechanism involving intramolecular chain transfer processes, especially those for the secondary alkyl radicals, could account for the formation of these compounds very well.

The pyrolytic products identified in this work were quite different from those observed by other investigators. The principle difference was that in this study, the volatile products were rapidly flushed away by the inert carrier gas. This condition perhaps better simulates the situation at the surface of a burning polymer.

Acknowledgement

The author would like to thank Dr. C.M. Wright of Hercules Incorporated for supplying the Profax 6501 polypropylene sample.

References

1. Volans, P., Conference on Flame Resistance in Polymers, London, 1966

2. Burge, S.J., Tipper, C.F.H., Combustion and Flame, 13, 495, 1969

3. Stuetz, D.E., Barnes, B.P., DiEdwardo, A.H., Zitomer, F., Polymer Conference Series, University of Utah, June 15-20, 1970

4. Chien, J.C.W., Wang, D.S.T., Macromolecules, 8, 920, 1975

5. Wright, C.M., Hercules Incorporated, private communication

6. Dietz, W.A., J. Gas Chromato., 68, 1967

7. Tomita, K., Polymer, 17, 221, 1976

8. Wall, L.A., Straus, S., J. Polymer Sci., 44, 313, 1960

9. Wall, L.A., 'High Temperature Resistance and Thermal Degradation of Polymers', S.C.I. Monography No. 13, Macmillian Co., N.Y., 145, 1961

10. Madorsky, S.L., Straus, S., J. Res. NBS, 53, 361, 1954

11. Straus, S., Wall, L.A., J. of Res. NBS, 65A, 221, 1961

12. Madorsky, S.L., J. Res. NBS, 62, 219, 1959

13. Moiseev, V.D., Neiman, M.B., Kriukova, A.I., Vysokomolekul. Soedin., 1, 1552, 1959

14. Madorsky, S.L., 'Thermal Degradation of Organic Polymers', Interscience, N.Y., 1964

15. Tsuchiya, Y., Sumi, K., J. Poly. Sci., A-1, 7, 1599, 1969

16. Bailey, W.J., Liotta, C., Polymer Preprints, 5, 333, 1964

17. Bailey, W.J., Proc. Symp. Polypropylene Fibers, Birmingham, Alabama, 121, 1964

18. Schooten, J. Van, Evenhuis, J.K., Polymer, 6, 343, 1965

19. Bresler, S.E., Osminskaya, A.T., Popov, A.G., Vysokomolekul.Soedin., 2, 930, 1960

20. Rice, F.O., Rice, K.K., 'The Aliphatic Free Radicals', Johns Hopkins Press, Baltimore, 1935

21. Kossiakoff, A., Rice, F.O., J. Am. Chem. Soc., 65, 590, 1943

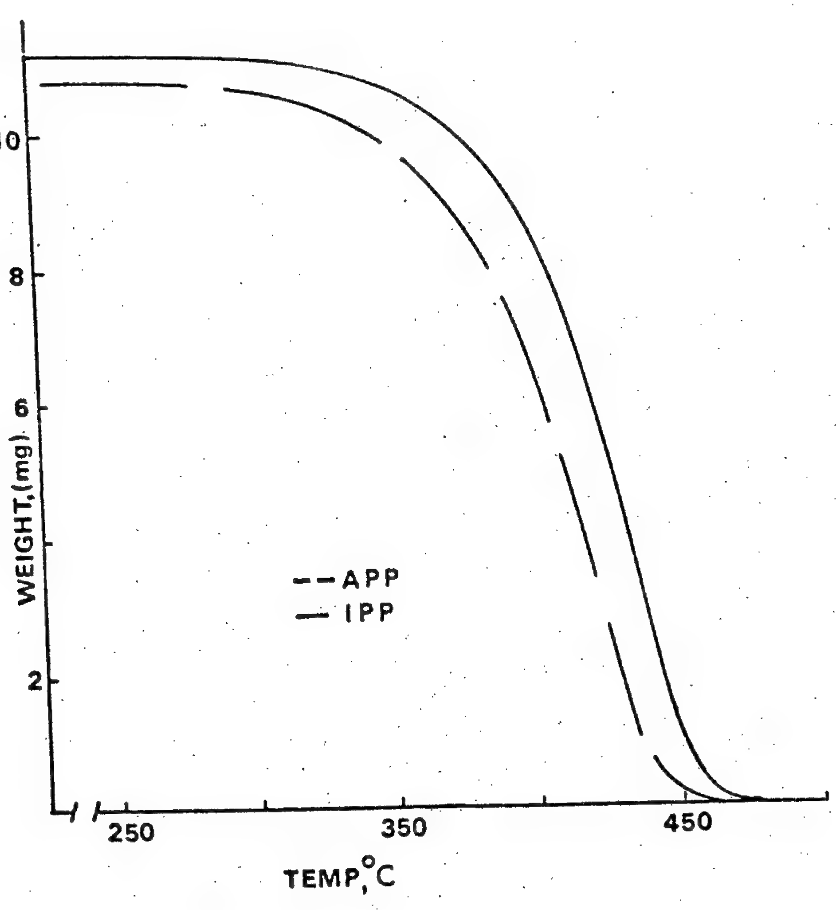


Fig. 1 TGA thermograms of APP and IPP in helium

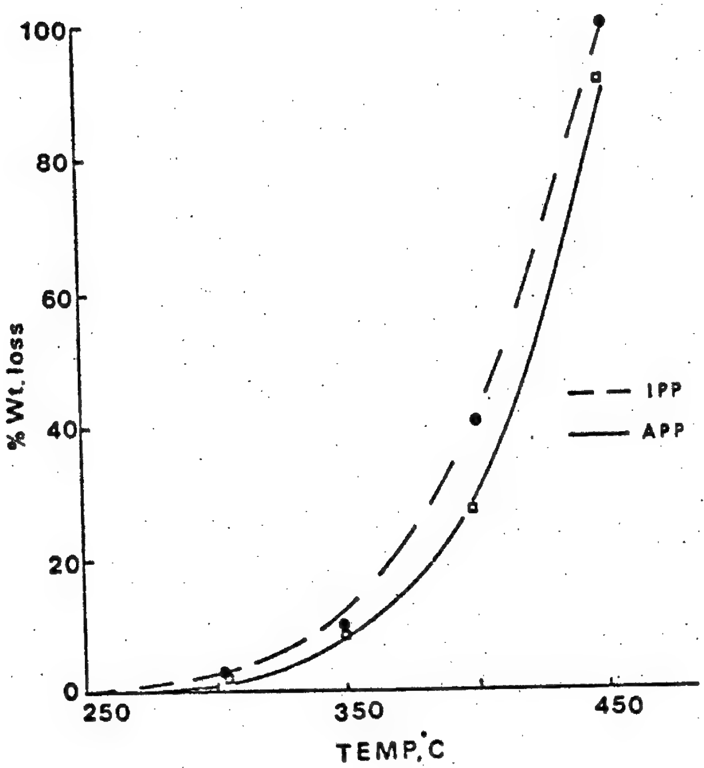


Fig. 2 Percent weight loss of APP and IPP in helium as a function of temperature

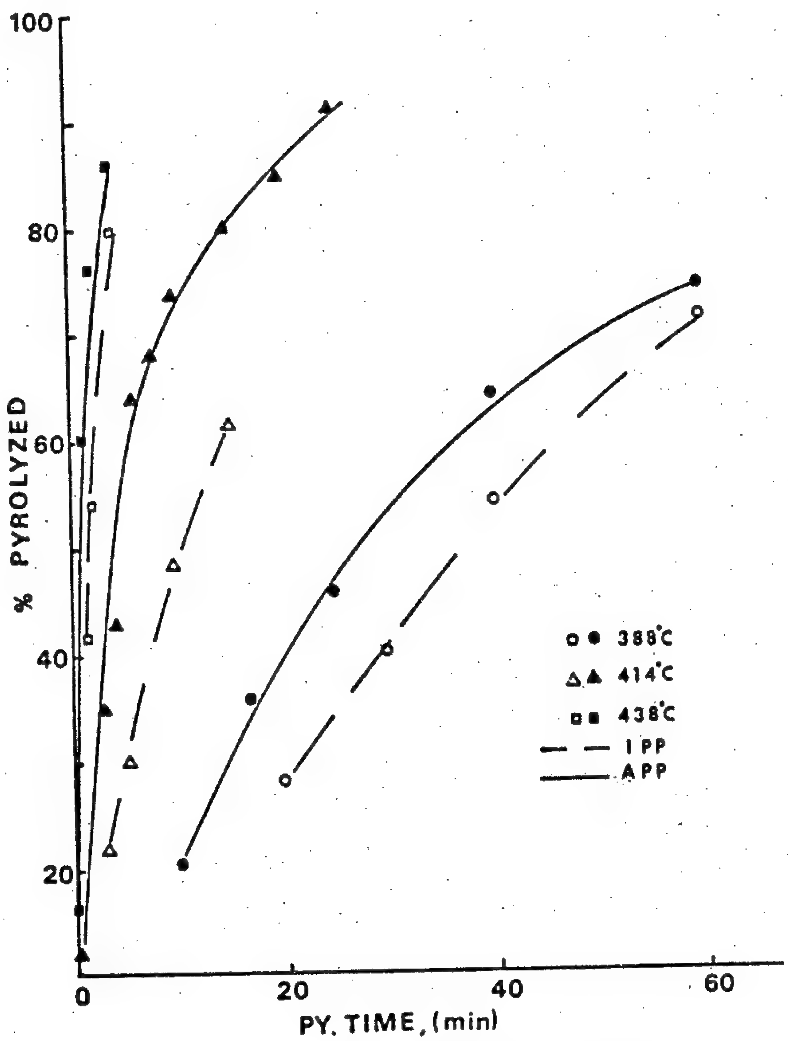


Fig. 3 Rates of pyrolysis of APP and IPP in helium at indicated temperatures

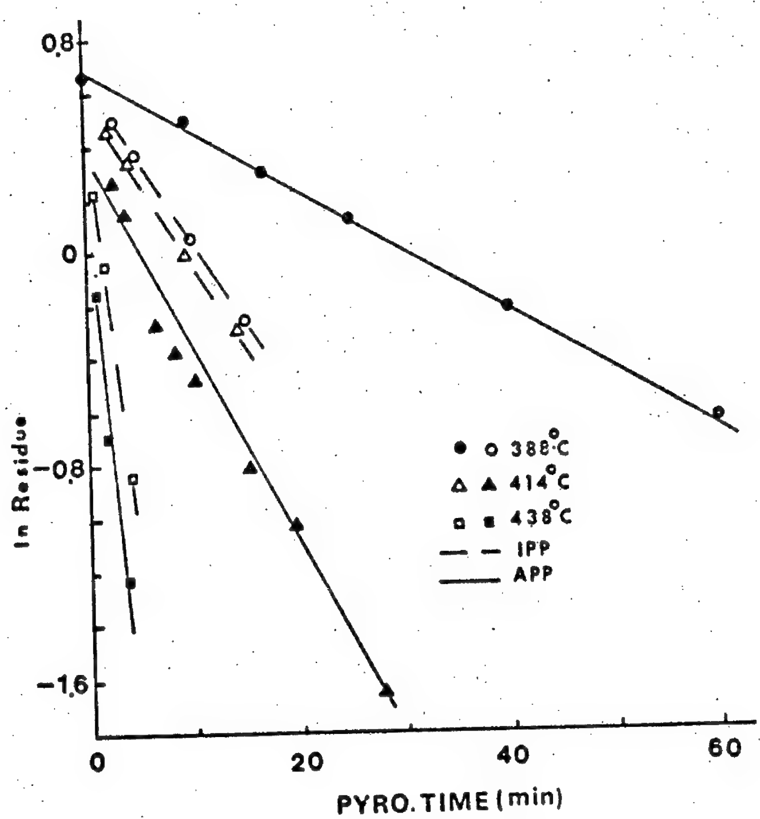


Fig. 4 First-order kinetic semilog plot of pyrolysis of APP and IPP in helium at indicated temperatures

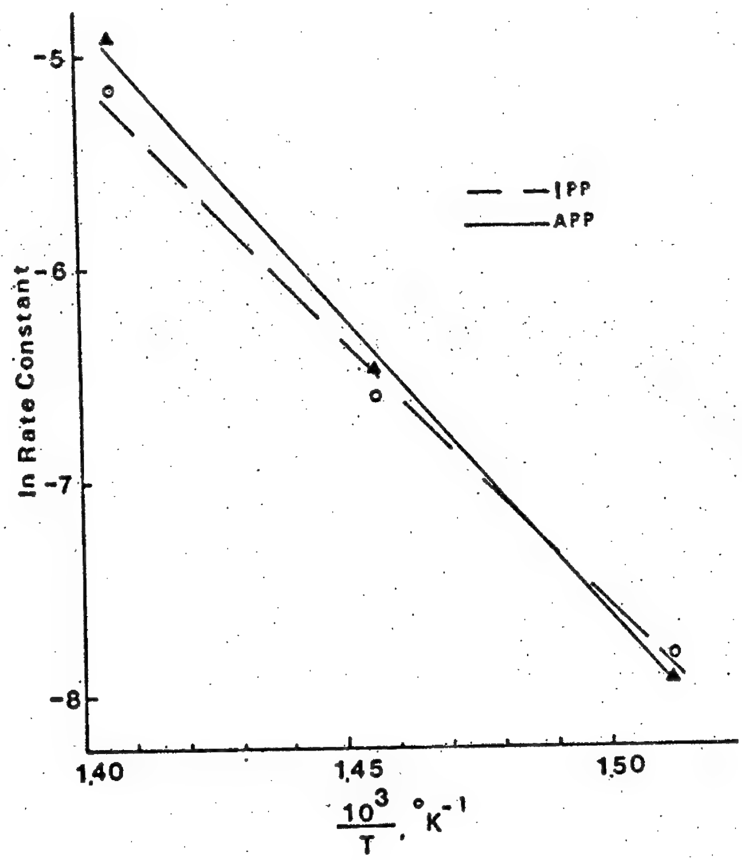


Fig. 5 Arrhenius plot for pyrolysis of APP and IPP in helium

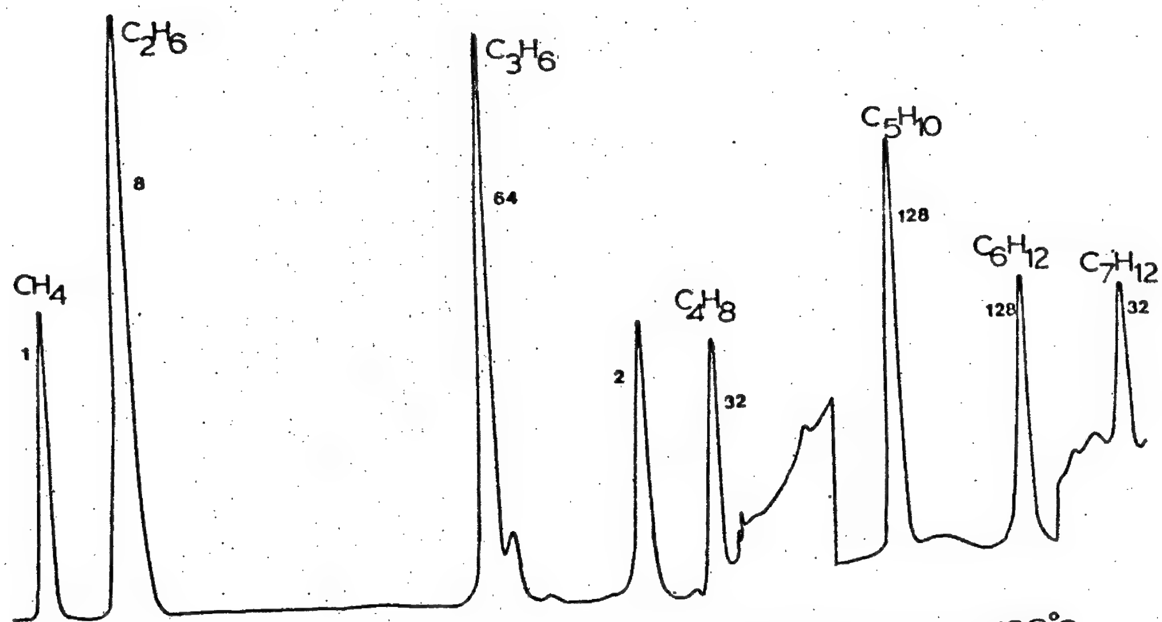


FIG.6 LOW-BOILING GC PYROGRAM OF IPP IN He AT 438°C

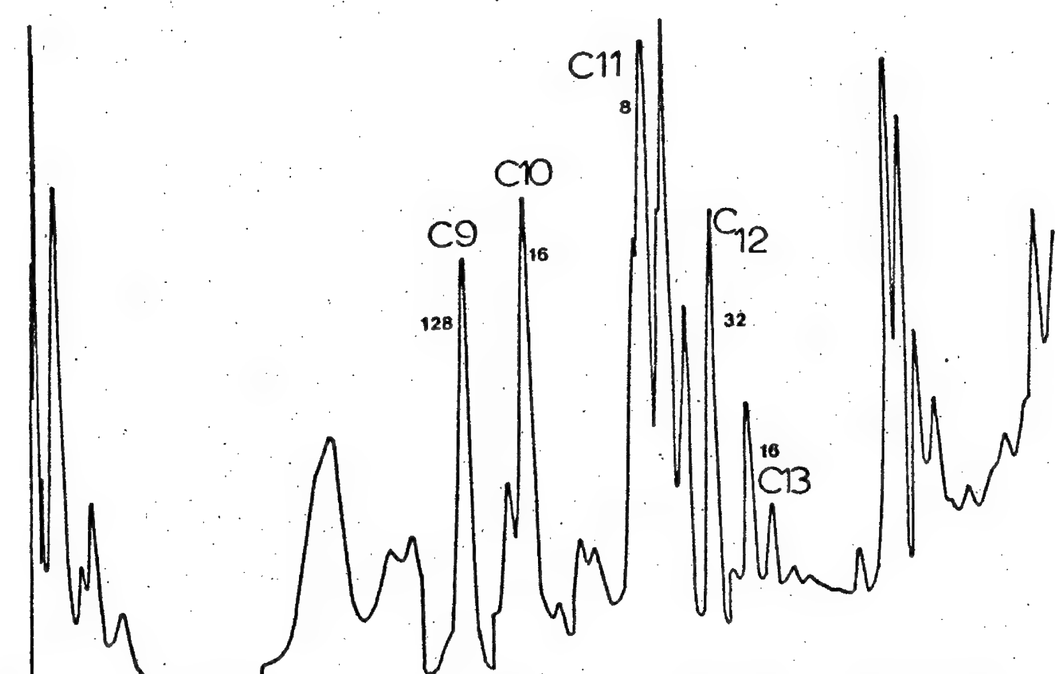


FIG.7 HIGH-BOILING GC PYROGRAM OF IPP IN He AT 438°C

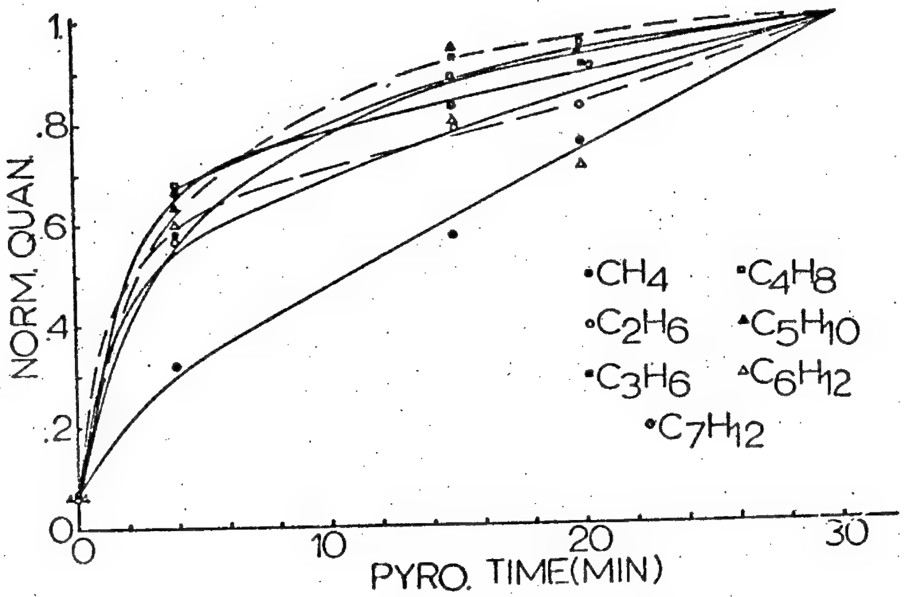


Fig. 8 Rates of formation of C_1 to C_7 hydrocarbons from pyrolysis of APP in He at 414°C as a function of pyrolysis time

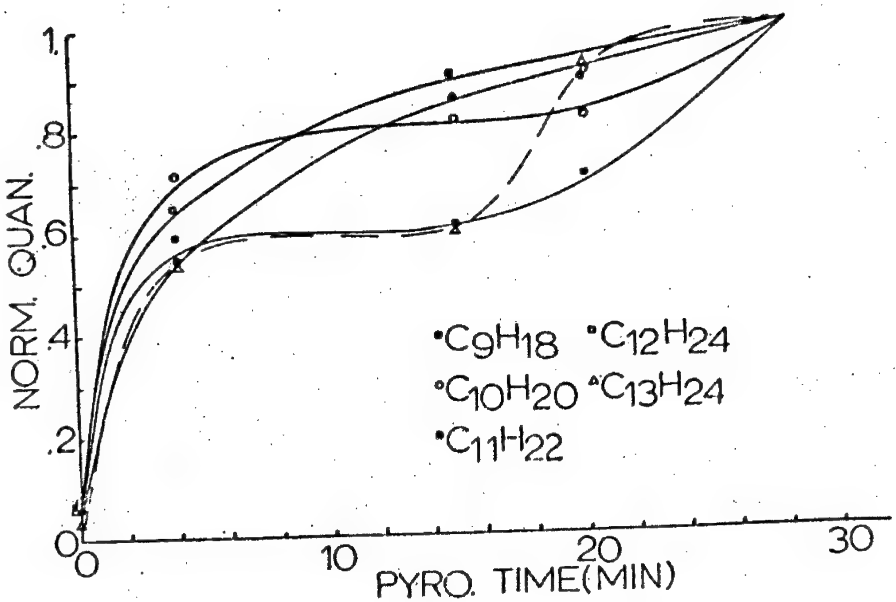


Fig. 9 Rates of formation of C_9 to C_{13} hydrocarbons from pyrolysis of APP in He at 414°C as a function of pyrolysis time

CHAPTER V

OXIDATIVE PYROLYSIS OF POLYPROPYLENE

Abstract

Amorphous and semi-crystalline polypropylene (APP and IPP) were pyrolyzed in air from 240°-289°C with a novel interfaced pyrolysis gas chromatographic peak identification system. The products were identified on-the-fly by rapid scan vapor phase infrared spectrophotometry and also by mass spectrometry. The major products were aldehydes, ketones, and a few hydrocarbons. Methanol was the only alcohol represented in significant amount. No carboxylic acid was found in any significant quantity.

The formations of major oxygenated products were diffusion controlled. At 289°C, they reached their maximum at about 4 percent oxygen and decreased rapidly as the oxygen concentration was increased. This is probably due to the enhanced oxidation of aldehydes and decarboxylation of subsequent acids. The oxidative pyrolysis of polypropylene followed first-order reaction kinetics and had an activation energy of about 16 Kcal $mole^{-1}$.

Finally, a simple mechanistic scheme was proposed which involved C-C scissions of the terminal and backbone alkoxy radicals accompanied by H· or ·CH_3 transfer and/or ·H abstraction to account for all of the products.

Introduction

When various polymers were burned in air in a 'candle-like' manner[1], whether the decomposition processes for the polymers are pure pyrolysis or oxidative pyrolysis is still largely unsettled.

It had been shown that the oxygen concentration 1 mm above the surface of a burning polyethylene rod was only about 1 percent[2]. Similar results were reported for polypropylene[3]. From this it may be inferred that the polymer in the melt surface may be oxygen depleted. On the other hand, the polymer further below the surface probably contains the usual amount of dissolved oxygen. It is likely that oxidative pyrolysis contributes significantly or even predominantly to the liberation of volatile and combustible fragments from the polymer. The relative importance of pure pyrolysis and oxidative pyrolysis can only be established by experimentation.

This Chapter is concerned with the oxidative pyrolysis of polypropylene. A novel interfaced pyrolysis gas chromatographic peak identification system(IPGCS) was used to analyze the products on-the-fly and their chemical structures were also determined by mass spectrometry.

Experimental

The APP and IPP used were the same as those employed in pure pyrolysis studies as presented in the previous Chapter.

Thermogravimetric analysis(TGA) for the two polypropylene samples at an air flow rate of 25 ml min^{-1} and a heating rate of $30^{\circ}C\ min^{-1}$ was performed with the DuPont 900 thermal analyzer.

Oxidative pyrolysis experiments were performed with the MP3 instrument of the IPGCS. About 5 mg of each sample was pyrolyzed at 240°, 264°, and $289^{\circ}C$ at a heating rate of $40^{\circ}C\ min^{-1}$ with an air flow rate of 25 ml min^{-1}. The products were collected and separated respectively by a Chromosorb 102 column (12 ft x 1/8" O.D.) and a Carbowax 20M on Chromosorb P column (12 ft x 1/8" O.D.). The former column was for low boilers and

the latter column for high-boiling products. The pyrograms were obtained with a thermal conductivity detector operating at 150 ma. At a helium carrier gas flow of 14 ml min^{-1}, the columns were temperature programmed at 4°C min^{-1} to 250°C. The products were identified on-the-fly by rapid scan vapor phase infrared spectrophotometry and by mass spectrometry in a similar manner as described in Chapter III (Experimental Techniques).

Similar procedures as described in the previous Chapter were employed for kinetic studies. The rate constants of decomposition at 240°, 264°, and 289°C were determined and the activation energies were obtained from the corresponding Arrhenius plot.

The product distributions of the pyrolysis of polypropylene as a function of oxygen concentration were investigated. In this experiment, IPP was pyrolyzed at 289° (5 minutes) at 1, 4, 20, 60 and 100 percent oxygen respectively. The products were separated by the Chromosorb 102 column and their distributions were studied as a function of oxygen concentration.

Results

Figure 1 shows the TGA curves in air for APP and IPP respectively. Figure 2 compares their corresponding weight loss versus temperatures. The rates of pyrolysis were obtained by weighing the polymer samples before and after pre-determined periods of pyrolysis time. The results are given in Figure 3. The pyrolysis processes follow first-order reaction kinetics as in thermal pyrolyses. Figure 4 shows the corresponding first-order kinetic semilog plot of the above results. Figure 5 shows the Arrhenius plots for the determination of the activation energies. The rate constants and activation energies for the oxidative pyrolysis of APP and IPP are compared in Table 1.

Table 1

Kinetic Results for the Oxidative Pyrolysis of Polypropylene

Temp, °C	Rate Constant, sec^{-1} APP	IPP
240	2.3×10^{-3}	2.5×10^{-3}
264	5.2×10^{-3}	5.4×10^{-3}
289	1.0×10^{-2}	9.2×10^{-3}
Activation Energy, Kcal $mole^{-1}$	17	15

The low-boiling pyrogram at 289°C obtained by the Chromosorb 102 column is shown in Figure 6. The numbers followed by x signs are the detector attenuation factors. The products in the order of increasing retention times are: 1) carbon dioxide, 2) ethylene, 3) ethane, 4) water, 5) propylene, 6) propane, 7) formaldehyde, 8) methanol, 9) acetaldehyde, 10) acrolein, 11) propan-1-al, 12) acetone, 13) 2 methylpropan-1-al, 14) methyl vinyl ketone, 15) butan-1-al, 16) pentan-2-one, 17) an unsaturated C_5 aldehyde, 18) an unsaturated C_6 ketone, and 19) 3-methyl 3,5 hexadiene. The number before each compound refers to the number of the peak in the pyrogram(compounds 1-4 were not shown).

The products were identified on-the-fly by rapid scan vapor phase infrared spectrophotometry and separately by mass spectrometry. The infrared spectra were compared to those complied by Welti[4]. The quality of the spectra is uniformly good as exemplified by that of acetone in Figure 7.

Table 2 shows the mass spectrometric fragmentation patterns of the oxidative pyrolysis products of IPP at 289°C. These patterns were compared to those in the literature. The underlined mass numbers were those

Table 2

Mass Spectrometric Fragmentation Patterns of the Oxidative Pyrolysis Products of IPP at 289°C (2 min)

Peak number	Molecular ion	Compound	Fragmentation Pattern
	44	Carbon dioxide	44, 28
	28	Ethylene	28, 27
	30	Ethane	30, 29, 28, 27, 26
	18	Water	18, 17, 16
5	42	Propylene	42, 41, 39, 27
6	44	Propane	44, 43, 29, 28, 27
7	30	Formaldehyde	30, 29, 28
8	32	Methanol	32, 31, 29, 15
9	44	Acetaldehyde	44, 43, 42, 29
10	56	Acrolein	56, 41, 39, 27
11	58	Propan-1-al	58, 43, 41, 29
12	58	Acetone	58, 43, 28
13	72	2-Methyl propan-1-al	72, 57, 43, 42, 41, 29, 27
14	70	Methyl vinyl ketone	70, 68, 67, 53, 42, 41, 40, 29, 27
15	72	Butan-1-al	72, 50, 42, 41, 39, 29
16	86	Pentan-2-one	86, 43, 29, 27
17	84	Unsat. C_5 aldehyde	84, 69, 56, 41, 39, 29, 27
18	98	Unsat. C_6 ketone	
19	96	3-Methyl 3,5 hexadiene	96, 81, 67, 53, 43, 41, 39

of the most abundant species. The peak numbers again refer to those shown in the pyrogram in Figure 5. The same products were formed at the other temperatures but with different distributions.

Figure 8 shows the distributions of the five major products from the oxidative pyrolysis of APP at 264°C. Figure 9 shows the distributions of the same products from the oxidative pyrolysis of IPP at 289°C. In these two figures, the absolute amount of each product, as measured from the area under peak, was normalized to itself at complete pyrolysis. Finally, Figure 10 shows the distributions of these five major products from the oxidative pyrolysis of IPP at 289°C as a function of oxygen concentration.

Discussion of Results

Autoxidation of polypropylene below its decomposition point (about 230°C; see Figure 1) has been much investigated[5-13]. In general, it is well known that molecular oxygen, because of its high reactivity towards possibly present free radicals, causes the formation of hydroperoxide groups, -OOH. As a result of the lability of the peroxide bond, these hydroperoxides tend to decompose with the formation of new free radicals which, in turn, again form hydroperoxides. Thus the reaction becomes autocatalytic.

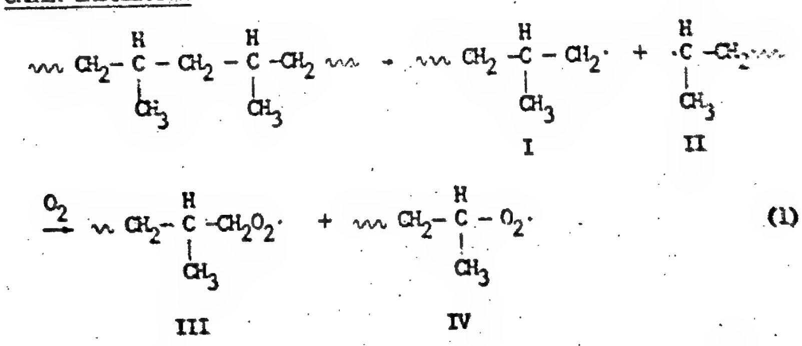
The formation of hydroperoxide groups creates the prerequisites for oxidative degradation of the polymer because the free radicals, formed by decomposition of these groups, can lead to chain scission.

Above the decomposition temperature, autoxidation of polypropylene leads to severe attack by oxygen on the polymer and extensive cleavage of C-C and C-H bonds results in free radicals which react rapidly with oxygen. Cullis et al.[14] studied the influence of hydrogen bromide on the autoxida-

tion of polypropylene at 430°C in a static and in a flowing stream of air. The process followed first-order reaction kinetics and was more relevant to the mechanism of the burning of the polymer. Product analysis, however, was limited only to aggregate yields of hydrocarbons and oxygenates.

Although very little fundamental work has been done on the high-temperature pre-flame autoxidation of polymers, a lot is known about the gas phase oxidation of hydrocarbons at high temperatures and the cool flame limit[15-18]. The reactions are recognized as free radical chain reactions propagated by peroxy radicals and hydroperoxides which is essentially a development of Bäckstrom's scheme for the oxidation of aldehydes[19]. These mechanisms can be adapted to the oxidative pyrolysis of polypropylene.

Chain Initiation

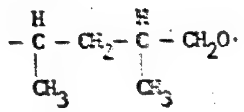


(1)

Chain Propagation

Radicals III and IV can extract a hydrogen atom intermolecularly to give the corresponding hydroperoxides of transient stability. Loss of ·OH leads to the respective alkoxy radicals V and VI. Scission of C-C bonds accompanied by H· or ·CH_3 transfer yields the products shown below where the numbers above the arrows indicate the particular C-C bond severed.

The underlined products correspond to those found in significant amounts experimentally.



V

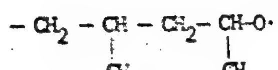
$$\xrightarrow{1,2} \text{II} + \text{formaldehyde}$$

$$\xrightarrow{2,3} \text{I} + \text{propan-1-al} + \text{acetaldehyde} + \text{ethylene}$$

$$\xrightarrow{3,4} \text{II} + \text{2-methyl-propan-1-al} + \text{propan-1-al} + \text{ethylene} \qquad (2)$$

$$\xrightarrow{4,5} \text{I} + \text{2-methyl-pentan-1-al} + \text{butan-1-al} + \text{ethylene}$$

$$\xrightarrow{5,6} \text{II} + \text{2,4 dimethyl-pentan-1-al}$$



VI

$$\xrightarrow{1,2} \text{I} + \text{acetaldehyde}$$

$$\xrightarrow{2,3} \text{II} + \text{acetone} + \text{propan-1-al}$$

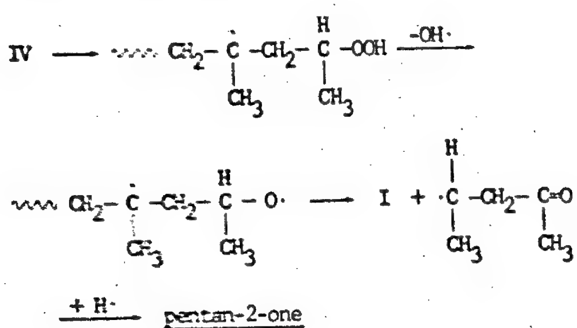
$$\xrightarrow{3,4} \text{I} + \text{pentan-2-one} + \text{3 methyl-butan-1-al} + \text{methyl vinyl ketone} + \text{methane} + \text{butan-1-al} + \text{ethylene} \qquad (3)$$

$$\xrightarrow{4,5} \text{II} + \text{4-methyl-pentan-2-one} + \text{3-methyl-pentan-1-al}$$

$$\xrightarrow{5,6} \text{I} + \text{4-methyl-heptan-2-one} + \text{3,5 dimethyl-hexan-1-al}$$

The formation of hydrocarbons can be accounted for by intramolecular chain transfer processes involving the primary(I) and secondary(II) alkyl radicals in a similar manner as shown in Chapter IV (Equations 3 and 4). Another source for hydrocarbons is probably from the decarboxylation of acids since the latter compounds were not identified and a lot of CO_2 was detected. Methanol is probably formed by Radical V by a hydrogen transfer process.

In addition, intramolecualr hydrogen abstraction, followed by loss of $\cdot OH$, C-C scission, $\cdot H$ or $\cdot CH_3$ transfer and $\cdot H$ abstraction[19-25] can lead to the same products of reactions 2 and 3. This is illustrated for abstraction of γ-H by Radical IV.



(4)

No attempt was made to identify the high boiling products, however, basing on the products identified, the following conclusion can be drawn. The primary alkoxy Radical V was responsible for the formation of aldehydes, all of the predicted aldehydes were identified in this study. Some of the aldehydes were also formed from the secondary peroxy Radical VI which was primarily responsible for the formation of ketones. C_3, C_4 and C_5 ketones were predicted and they were all identified.

A few unsaturated carbonyl compounds were observed although they are not expected under the experimental conditions prescribed in this study (small sample under a flowing stream of air).

Normally for small sample under a rapid flowing stream of air all of the alkyl radicals will react immediately with oxygen before any other chemical processes, such as isomerization and dissociation, can occur. For bulk polymer this will not be true. Then intramolecular chain transfer

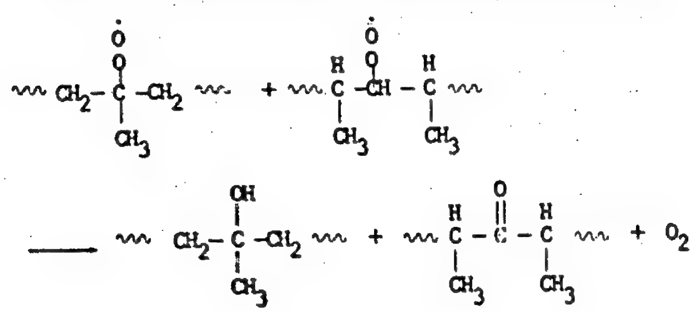
and chain propagation processes of Radicals I, II, V and VI become important, their relative significance being governed by the local oxygen concentrations. These will lead to unsaturated carbonyl products.

Since the sample used in this work was small, the only plausible explanation is that the flow rate (25 ml min^{-1}) is not rapid enough to flush away some of the products once they were formed.

It should be pointed out that whereas the terminal radicals are responsible for the volatile products observed, similar reactions occur for the backbone radicals. The backbone tertiary or secondary peroxy radicals can isomerize by H-transfer from β, γ, or δ carbons intramolecularly. Subsequent reactions are: loss of HO· produces O-heterocycles such as oxinan, furan and pyran[20-22]; loss of HO· with C-C bond scission, group migration and H-abstraction forms carbonyl compounds with rearranged polymer backbone[23-25]; loss of HO· with C-C bond scission and H-transfer leads to terminal carbonyl and olefinic functionalities; and loss of HO_2· produces internal double bonds[26]. The backbone peroxy radicals can also isomerize via group transfer[27,28] followed by O-O bond scission to give internal and terminal carbonyl compounds as well as low molecular weight and high molecular weight alkoxy radicals.

Chain Termination

This occurs undoubtedly by bimolecular process such as,



(5)

The effect of oxidation of polypropylene at elevated temperature (289°C) as a function of oxygen concentration had been investigated as shown in Figure 10. It is interesting to note that the formations of the major oxygenated products such as acetone, acetaldehyde and butan-1-al were diffusion controlled. At 289°C, these products attained their maximum quantities at about 4 percent oxygen and decreased rapidly as the oxygen concentration was increased.

On the other hand, the formation of CO_2 increased rapidly also from about 4 percent oxygen concentration. This is probably due to the enhanced oxidation of aldehydes and decarboxylation of the subsequent acids. The increased formation of propylene, the major hydrocarbon product, with increased oxygen concentration can also be explained by the above phenomena.

The fact that the formations of ketones and aldehydes are favored at low oxygen concentration aggravates the effect of simultaneous oxygen depletion and temperature rise which has been the major cause of fire deaths.

Conclusion

A novel interfaced pyrolysis gas chromatographic peak identification system had been used to study the oxidative pyrolysis of polypropylene at temperatures between 240°-289°C.

The products were identified on-the-fly by rapid scan vapor phase infrared spectrophotometry and also by mass spectrometry. The major products were aldehydes and ketones together with a few hydrocarbons. Methanol was the only alcohol represented. No carboxylic acids were present in any significant amount to be identified. The formation of hydrocarbons

could be either due to intramolecular chain transfer processes involving the primary and secondary alkyl radicals as in thermal pyrolysis or to the decarboxylation of acids.

This study had shown that the formation of main oxygenated products from the oxidative pyrolysis of polypropylene was diffusion controlled. At 289°C, these products attained their maximum concentrations at about 4 percent oxygen and decreased rapidly as the oxygen concentration was increased. The increase of oxygen concentration enhanced the oxidation of aldehydes and the decarboxylation of subsequent acids led to the increase of CO_2 formation.

The oxidative pyrolysis of polypropylene at temperatures between 240°-289°C followed first-order reaction kinetics and an activation energy of about 16 Kcal mole^{-1} was obtained. Finally, a simple mechanistic scheme was proposed which involved C-C scissions of the terminal and backbone alkoxy radicals accompanied by ·H or ·CH_3 transfer and/or ·H abstraction to account for all of the identified products.

References

1. Volans, P., Conference on Flame Resistance in Polymers, London, 1966

2. Burge, S.J., Tipper, D.F.H., Combustion and Flame, 13, 495, 1969

3. Stuetz, D.E., Barnes, B.P., DiEdwardo, A.H., Zitomer, F., Polymer Conference Series, University of Utah, June 15-20, 1970

4. Welti, D., 'Infrared Vapor Spectra', Heyden Sadtler, 1970

5. Hawkins, W.L., Matreyek, W.W., Winslow, F.H., J. Polymer Sci., 41, 1, 1959

6. Monaci, A., Lazzri, P., Berarducci, E., Chimica e Industria, 45, 1337, 1963

7. Stivala, S.S., Reich, L., Polymer Eng. Sci., 5, 179,1965

8. Ladrnicek, B.R., Stivala, S.S., Reich, L., J. App. Polymer Sci., 14, 25, 37, 1970

9. Chien, J.C.W., Vandenberg, E.J., Jabloner, H., J. Polymer Sci., A-1, 6, 381, 1968

10. Chien, J.C.W., Jabloner, H., J. Polymer Sci., A-1, 6, 393, 1968

11. Chien, J.C.W., Boss, C.R., J. Polymer Sci., A-1, 5, 3071, 1967

12. Chien, J.C.W., Boss, C.R., J. Polymer Sci., A-1, 5, 1683, 1967

13. Chien, J.C.W., Wang, D.S.T., Macromolecules, 8, 920, 1975

14. Cullis, C.F., Groome, I.J., Carabine, M.D., Proc. Roy. Soc. London, 324, 217, 1971

15. Ubbelohde, A.R., Proc. Roy. Soc. A, 152, 354, 1935

16. Hinshelwood, C.N., Disc. Faraday Soc., 2, 117, 1947

17. Walsh, A.D., Trans. Faraday Soc., 42, 269, 1946

18. Norrish, R.G.W., Disc. Faraday Soc., 10, 269, 1951

19. Bäckstrom, H.L.J., J. Am. Chem. Soc., 49, 1460, 1927

20. Bailey, H.C., Norrish, R.G.W., Proc. Roy. Soc. A, 212, 311, 1952

21. Kyryacos, G., Menapace, H.R., Boord, C.E., Anal. Chem., 31,222, 1959

22. Chung Y.H., Sandler, S., Combustion and Flame, 6, 295, 1962

23. Trimm, D.L., Cullis, C.F., J. Chem. Soc., 1430, 1963

24. Cullis, C.F., Hardy, F.R.F., Turner, D.W., Proc. Roy. Soc. A, 251, 265, 1959

25. Raley, J.H., Rust, F.F., Vaughan, W.E., J. Am. Chem. Soc., 70, 88, 1948

26. Zeelenberg, A.P., Bickel, A.F., J. Chem. Soc., 4014, 1961

27. Zeelenberg, A.P., Rec. Trav. Chim., 81, 720, 1962

28. Semenov, N.N., 'Some Problems of Chemical Kinetics and Reactivity', Pergamon Press, London, 1, 99, 1958

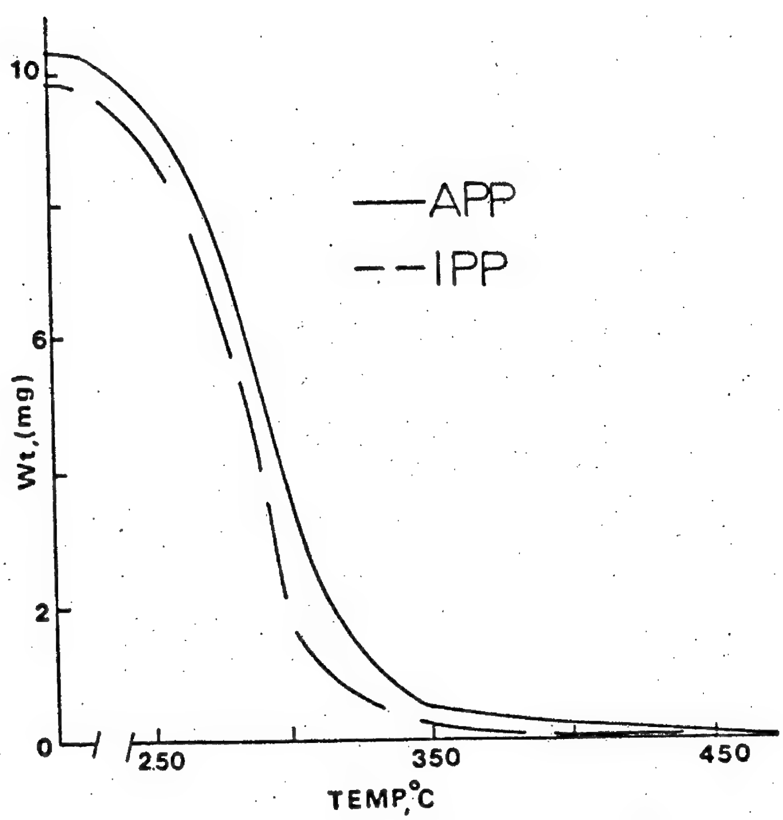


Fig. 1 TGA thermograms of APP and IPP in air

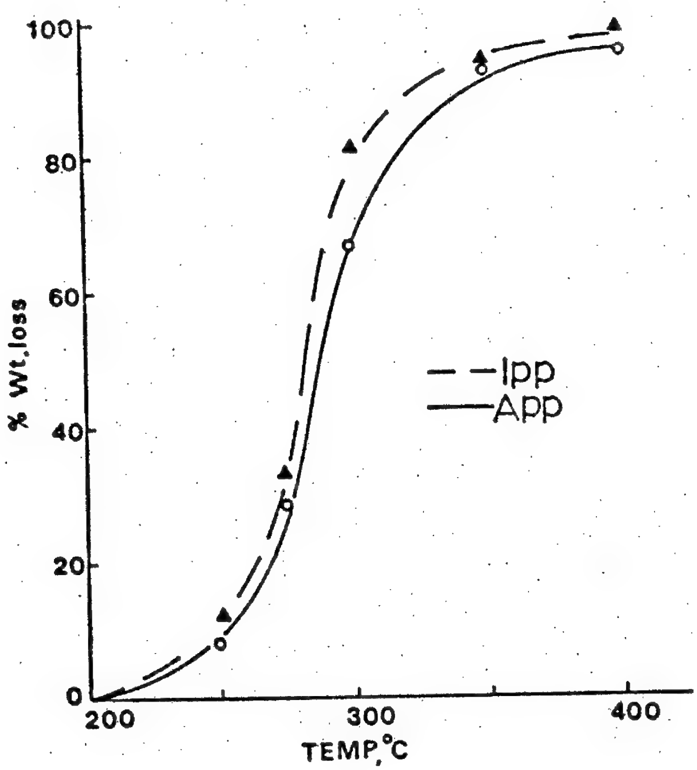


Fig. 2 Percent weight loss of APP and IPP in air as a function of temperature

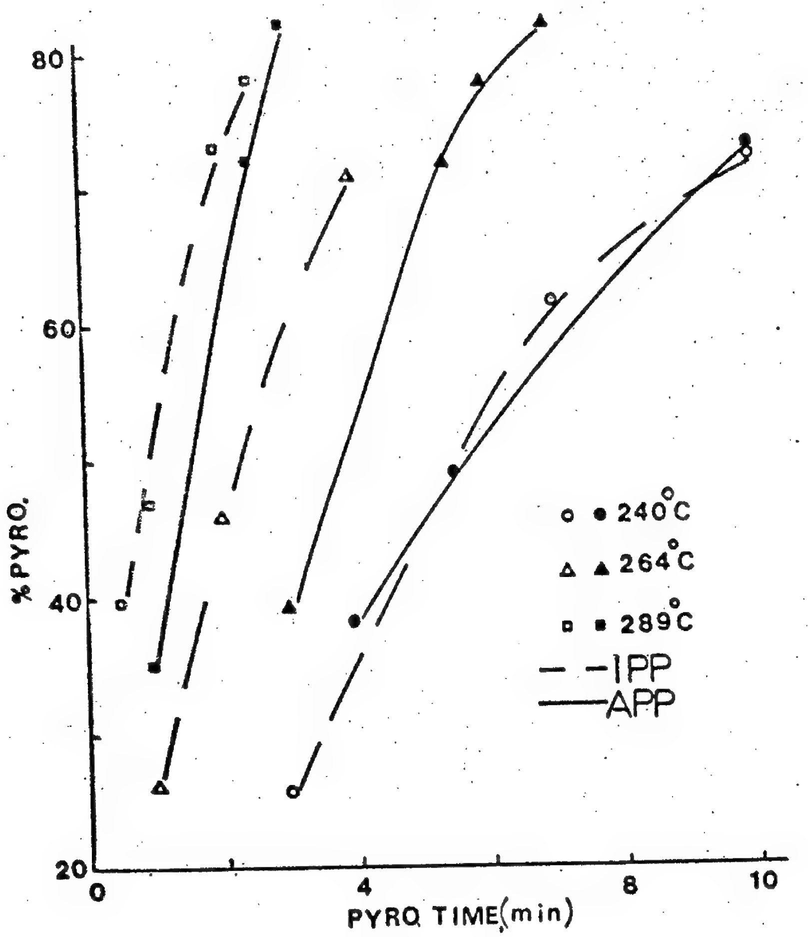


Fig. 3 Rates of pyrolysis of APP and IPP in air at indicated temperatures

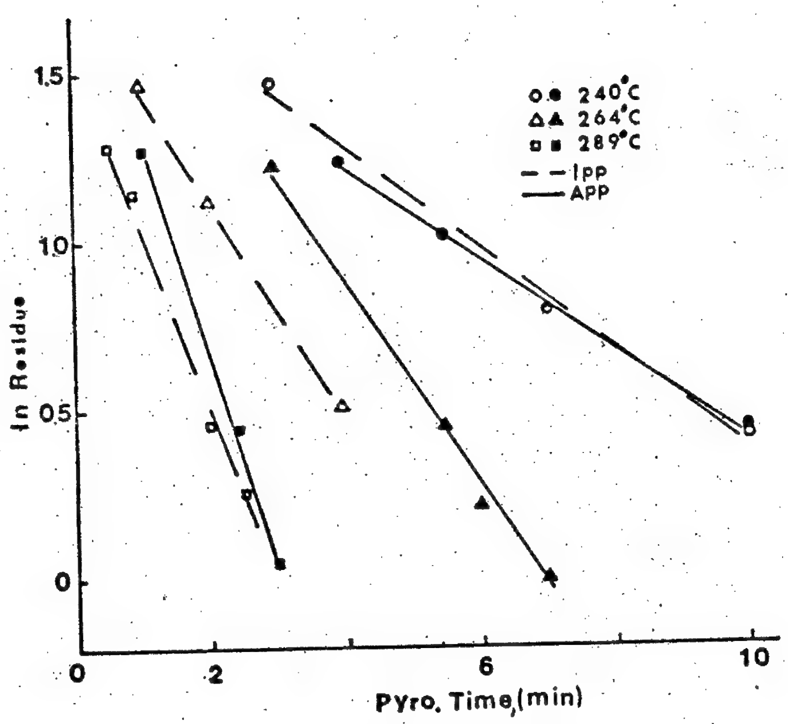


Fig. 4 First-order kinetic semilog plot of pyrolysis of APP and IPP at indicated temperatures

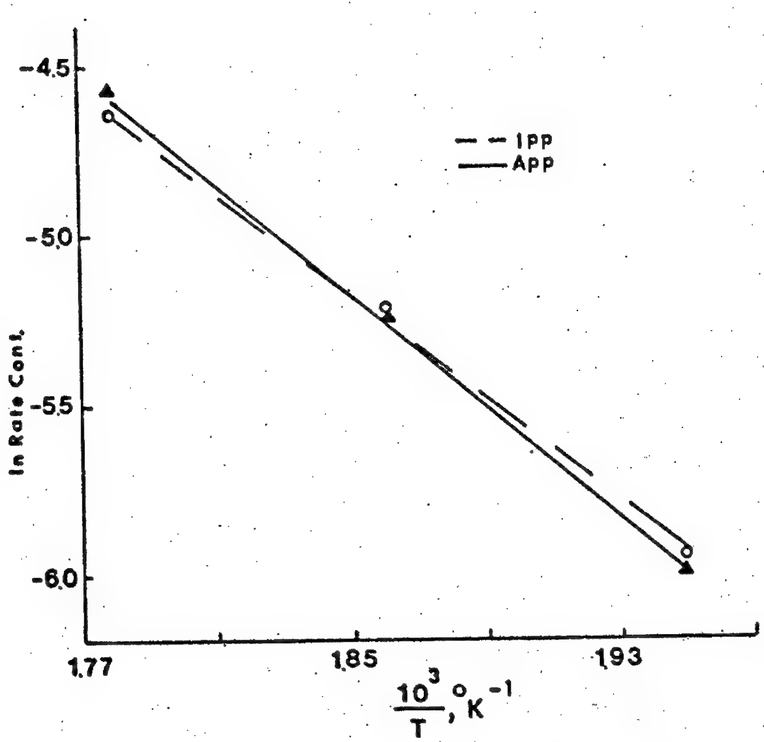


Fig. 5 Arrhenius plot for pyrolysis of APP and IPP in air

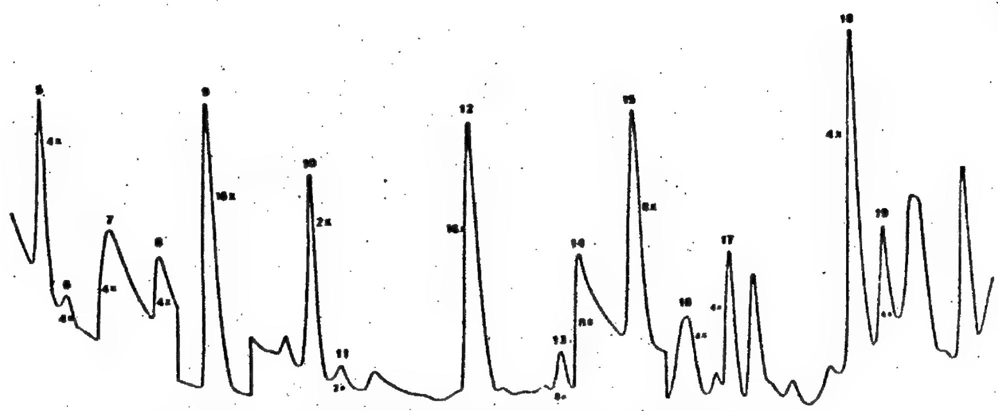


FIG.6 LOW BOILING GC PYROGRAM OF IPP IN AIR AT 289°C

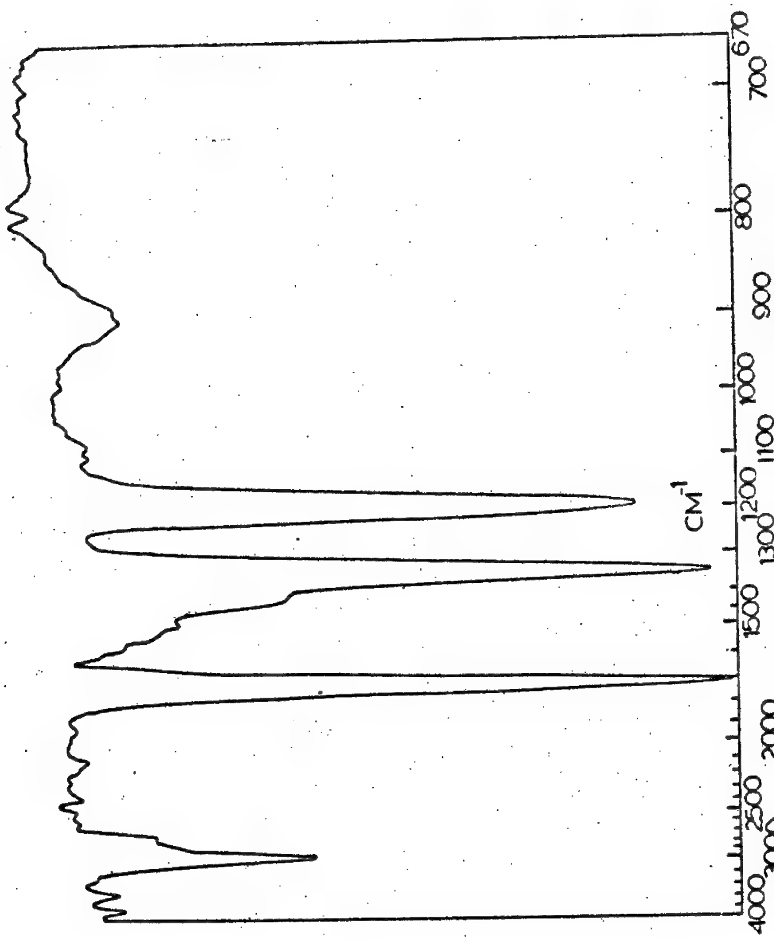


FIG.7 6 SEC SCAN OF VAPOR PHASE IR OF ACETONE

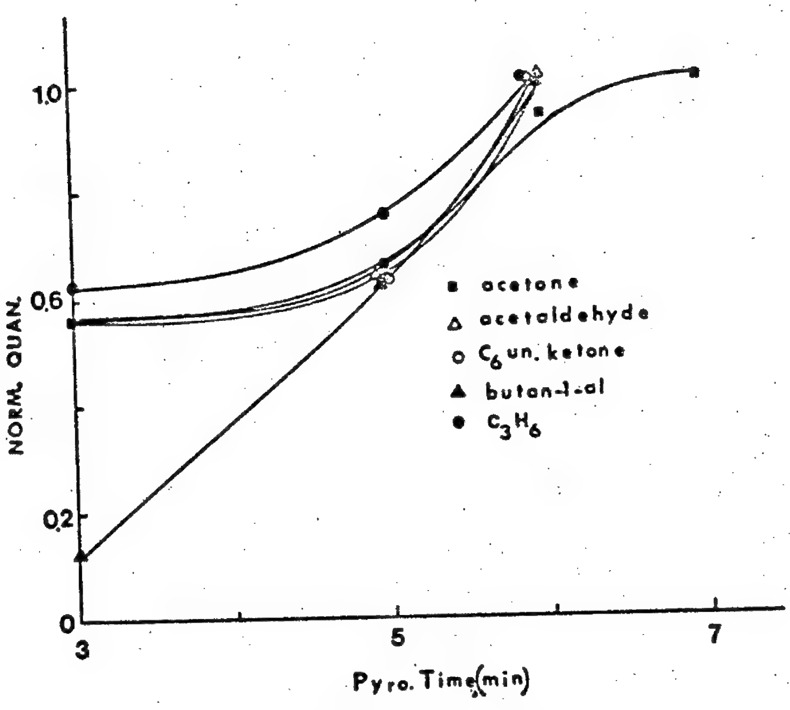


Fig. 8 Normalized distributions of major products from pyrolysis of APP in air at 264°C as a function of pyrolysis time

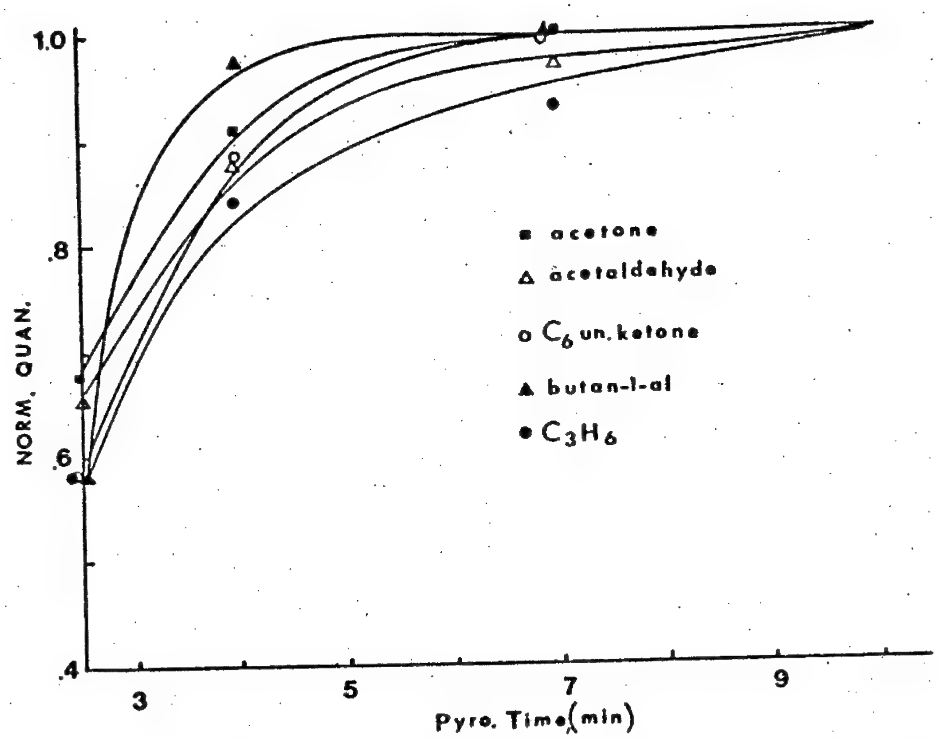


Fig. 9 Normalized distributions of major products from pyrolysis of IPP in air at 289°C as a function of pyrolysis time

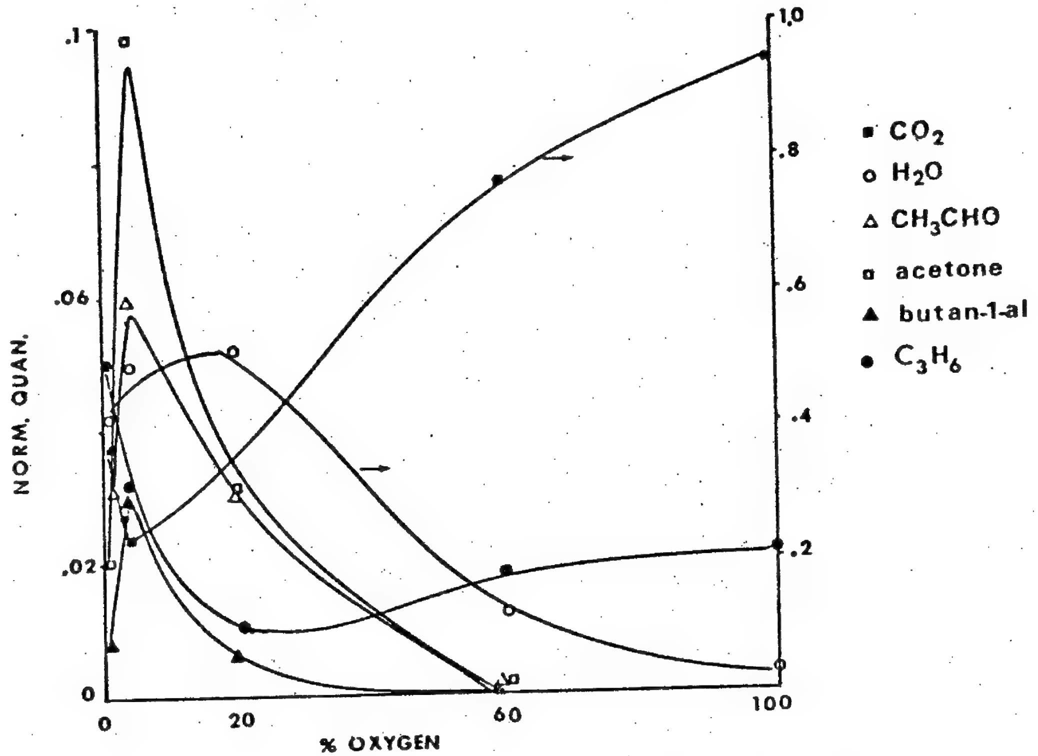


Fig. 10 Normalized distributions of major products from pyrolysis of IPP in air at 289°C as a function of oxygen concentration

CHAPTER VI

EFFECT OF CHROMIUM ON THE PYROLYSIS AND OXIDATIVE PYROLYSIS OF POLYPROPYLENE

Abstract

Semi-crystalline isotactic polypropylene(IPP) was reacted with chromyl chloride(CrO_2Cl_2) in an Etard reaction. Samples containing different concentrations of chromium and chlorine were prepared under different experimental conditions. A novel interfaced pyrolysis gas chromatographic peak identification system was used to pyrolyze the chromium-containing polypropylene in inert and in oxidative atmospheres. The processes followed first-order reaction kinetics. The corresponding rate constants of decomposition and activation energies were compared to those obtained for IPP. The presence of chromium in the polymer was found not to affect the nature of the products in both polymers.

In inert atmosphere, the polypropylene with chromium decomposed faster than polypropylene itself and exhibited a lower activation energy (44 Kcal $mole^{-1}$ vs 51 Kcal $mole^{-1}$). In oxidative environment, chromium induced char formation and inhibited pyrolysis resulting in a higher activation energy than the neat polypropylene(26 Kcal $mole^{-1}$ vs 16 Kcal $mole^{-1}$). The inhibitive effect was greater the higher the pyrolysis temperature studied.

The polypropylene samples with chromium and chlorine were also investigated for their thermal stabilities and ignition characteristics by thermogravimetric analysis(TGA) and differential thermal analysis(DTA). Their relative flammabilities were studied by the limiting oxygen index (LOI) test. The role of chromium and chlorine in flame inhibition is

believed to be due to free radical scavenging to form stable compounds, thus stopping flame propagation.

Introduction

To obtain flame retarded polymers, several approaches are available. One is to synthesize new polymers which contain few or no aliphatic hydrogens and have very rigid or crosslinked structures. Thus polymers such as poly-m-phenylene, isophthalmide, Nomex, poly-N-N-(p-p-oxydiphenylene), pyromellitimide (Kapton), polybenzimidazole, and Kynol (crosslinked phenol formaldehyde) have greatly reduced flammability. Inorganic polymers provide another solution to the problem but they are inherently expensive and difficult to process.

Modification of commodity polymers is yet another way to obtain flame retardation. This can be achieved by either the additive or the reactive approach. In the first method, the additive is usually a flame retardant system comprised of halogens, antimony and phosphorus containing compounds. The efficiency of a system is enhanced if the constituents function synergistically and are formulated in optimum ratios. The reactive approach is more efficient in flame retardation but less economical to use.

Present flame retardants are at best stop-gap measures. The add-on levels are in the range of 10 to 30 parts per hundred. They contribute towards the emission of noxious gases in addition to those derived from the substrate. An ideal system should then be one that requires a low dosage of additive to render flame retardancy.

There have been a lot of studies on the stabilization of polypropylene with regards to its thermal and thermoxidative degradation. Moiseev et al.[1] observed that the inclusion of 1 percent by weight of diphenyl propane into polypropylene decreased the rate of decomposition in vacuum by 4 percent. At 5 percent level, the rate was reduced by 90 percent. Straus and Wall[2] also observed that the introduction of minute quantities of inorganic and organic materials into polypropylene increased the thermal stability of the polymer in vacuum by lowering the rates of decomposition and increasing the activation energy. No explanation was given for the observed phenomena.

In thermoxidative degradation, stabilizers such as amine,phenols, ketonic compounds, metal and phosphorus containing compounds have been used[3-12]. In general, hydrogen donating chain stabilizers are used to interrupt chain depropagation through the formation of stable radicals in a chain transfer process[13].

In this study, the use of metal-containing compounds is of primary interest in pyrolysis inhibition. IPP was reacted with chromyl chloride and the samples were examined for pyrolysis, oxidative pyrolysis, thermal stabilities, ignition characteristics, and relative flammabilities. The results were compared to those obtained for neat IPP.

Experimental

Sample Preparation

Profax 6501 IPP (Hercules Inc.) was reacted with chromyl chloride (CrO_2Cl_2) in an Etard reaction[14,15]. Sample A was prepared as followed. About 5.2 gm of IPP was swollen with stirring in a 1000 ml three neck round-bottomed reaction flask in 100 ml of CCl_4 for 15 hours. About 1 ml (12.4 mmole) of CrO_2Cl_2 was dissolved in 60 ml of degassed dry CCl_4 in a glove bag flushed with nitrogen. The solution was quickly transferred to a dripping funnel fitted to the reaction flask which was purged continuously with nitrogen. The CrO_2Cl_2 solution was then added dropwise to the well-stirred swollen polymer in CCl_4. The reaction mixture was allowed to stand for about 15 hours. The product was filtered, washed with CCl_4 and vacuum dried at 80°C for 40 hours.

Samples B and C were similarly prepared. The general procedures were the same except for the degree of swelling and stirring of the polymer before and after the reaction. Sample B was prepared by reacting 2 ml(24.6 mmole) of CrO_2Cl_2 with about 103 gm of IPP. The latter polymer was swollen in CCl_4 at 50°C with stirring for 2 days before use. The final reaction mixture was slightly stirred for 15 hours.

In preparing Sample C, 10 ml(131 mmole) of CrO_2Cl_2 was used to react with about 304 gm of IPP. In this experiment, IPP was swollen with agitation in about 780 ml of CCl_4 for 5 days and the final reaction mixture was vigorously stirred, also for 15 hours. Samples A and C were greenish in color while Sample B was light-green.

Pyrolysis in Inert Atmosphere

Pyrolysis and TGA of Sample A were performed in a similar manner as described for IPP in Chapter IV. About 2 mg of sample was used in each pyrolysis experiment at 388°, 414°, and 438°C and for different periods of time. The products were similarly collected and pyrograms obtained with the same columns by temperature programming. The pyrolysis process was found to follow first-order reaction kinetics. The rates of decomposition and the activation energy for the pyrolysis process were determined and compared to those obtained for IPP. Product distributions at 438°C were examined.

DTA was performed on Sample C with the DuPont 950 plug-in module at a nitrogen flow of 60 ml min^{-1} and a heating rate of 10°C min^{-1}. The experiment was repeated with an IPP sample of similar size (9 mg) for comparison.

Oxidative Pyrolysis

Oxidative pyrolysis and TGA of Sample A in air were performed in a similar manner as described for IPP in Chapter V. About 5 mg of sample was used in each pyrolysis experiment at 264°, 289°, 313° and 338°C and for different periods of time. The products were similarly collected and pyrograms obtained with the same columns by temperature programming. A first-order reaction kinetics was again found for the pyrolysis process. The rates of decomposition and activation energy for the process were determined and again compared to those obtained for IPP in Chapter V.

Product distributions and absolute amount of total volatiles (up to C_6 oxygenates and C_7 hydrocarbons) were examined at 240°, 264°, and 289°C. DTA of Sample C at an air flow rate of 60 ml min^{-1} and a heating rate of

$10^{\circ}C\ min^{-1}$ was conducted. The results obtained from IPP under similar conditions were used for comparison.

The thermal behaviors of Sample A and IPP were also compared in pure oxygen. The self-ignition temperatures of these samples were investigated by TGA at an oxygen flow of 25 ml min^{-1} and a heating rate of $30^{\circ}C$ min^{-1}.

Sample A was pyrolyzed in pure oxygen between 240°-289°C in a similar manner as in air pyrolysis. First-order rate constants of decomposition and activation energy were determined. Under similar conditions, the pyrolysis of IPP often resulted in the ignition of the polymer.

Finally, for LOI studies, Sample B was divided into three portions. The first and the second portions were let-down 5 : 1 and 10 : 1 by weight (Samples D and E) respectively with neat IPP. The third portion was Sample B itself. Samples B, D, and E were compression molded at 230°C at 10,000 psi for 4 minutes in a 5" x 5" x 1/16" mold. The neat IPP was mixed by tumbling action prior to molding Samples D and E.

Results

Pyrolysis in Inert Atmosphere

Figure 1 shows the TGA curves in nitrogen for Sample A and IPP. Figure 2 compares the weight loss of the two polymers with respect to temperatures. The temperatures for 50 percent weight loss were about 400° and 385°C respectively for Sample A and IPP. About 3 percent sooty residue remained at 460°C for Sample A while IPP was completely pyrolyzed at 420°C.

The rate of pyrolysis of Sample A and IPP is shown in Figure 3. Figure 4 shows the corresponding first-order kinetic semilog plot of the residue versus pyrolysis time. Figure 5 compares the Arrhenius plots of the two polymers. Table 1 summarizes the results of the rate constants and activation energies for the pyrolysis of Sample A and IPP in inert atmosphere.

Table 1

Kinetic Results of Pyrolysis of Sample A and IPP in Helium

Temp, °C	Rate Constants, sec^{-1} Sample A	IPP
388	4.4×10^{-4}	4.0×10^{-4}
414	2.2×10^{-3}	1.1×10^{-3}
438	4.5×10^{-3}	6.2×10^{-3}
Activation Energy, Kcal $mole^{-1}$	44	51

The pyrolytic products of Sample A were similar to those obtained for IPP. Table 2 compares the relative product distributions of Sample A and IPP at 438° C(4 minutes). In this Table, the relative weight percent of each product was obtained by normalizing with respect to the total volatiles (up to C_{13}) according to the method by Dietz[16]. Figure 6 shows the absolute normalized product distributions (absolute amounts on pyrograms) for Sample A and IPP at 438° C.

Figure 7 compares the DTA of Sample C and IPP in nitrogen. Finally, Figure 8 shows the weight loss of these two polymers versus temperatures.

Table 2

Relative Product Distributions of Sample A and IPP at 438°C

	Relative Weight Percent	
	Sample A	IPP
Methane	0.38	0.1
Ethane	0.80	1.0
Propylene	12.0	10.0
Isobutylene	6.1	2.5
Pentene	12.0	14.0
3 methyl-1-pentene	7.0	9.4
3 methyl-3,5 hexadiene	3.3	1.6
2,4 dimethyl-heptene	36.0	40.0
$C_{10}H_{20}$	5.8	2.1
4,6 dimethyl-3-nonene	1.6	1.5
2,4,6 trimethyl-8-nonene	7.1	9.7
$C_{13}H_{24}$	1.0	1.8
unidentified	5.7	6.7

Oxidative Pyrolysis

Figure 9 shows that TGA curves in air for Sample A and IPP. Figure 10 compares the weight loss of these two polymers with respect to temperatures. In air, IPP was stable up to about 220°C under the prescribed experimental conditions in this study while Sample A exhibited about 7 percent weight loss. The temperatures for 50 percent weight loss were

about 425° and 325°C respectively for Sample A and IPP. The rates of pyrolysis and the corresponding first-order kinetic semilog plot are shown in Figures 11 and 12.

The major products from the oxidative pyrolysis of Sample A and IPP were acetaldehyde, acetone, butan-1-al, and an unsaturated C_6 ketone. The absolute amount of each of these products, as measured from the area under peak, from Sample A was normalized with respect to its corresponding peak from IPP. Hence, a ratio of one means the same amount of the same product are produced from both materials. Fractional quantities indicate suppression of products by Sample A.

The absolute normalized distributions of the above products from the oxidative pyrolysis of Sample A and IPP at 240°, 264°, and 289°C are shown in Figures 13, 14 and 15 respectively. These Figures compare the rates of product formation from Sample A with that of IPP itself. Figure 16 shows a similar plot of the rates of formation of the major products as a function of pyrolysis temperature. Figure 17 again shows a similar plot comparing the total amount of volatiles from Sample A and IPP as a function of pyrolysis temperature. Figure 18 shows the DTA of Sample C and IPP in air at a flow rate of 60 ml min^{-1}. Strong ignition exotherms were observed at 400° and 250°C for Sample C and IPP respectively.

The thermal behavior of Sample A was also studied in pure oxygen so as to elucidate the effect of oxygen concentration on pyrolysis inhibition. Figure 19 compares the TGA curves of Sample A and IPP in oxygen at a flow rate of 25 ml min^{-1}. The experiments were interrupted because of sudden weight losses due to ignitions of the two samples.

The rates of pyrolysis and subsequent first-order kinetic plot of Sample A are shown in Figures 20 and 21. Figure 22 shows the Arrhenius plot for the oxidative pyrolysis of Sample A and IPP.

Table 3 compares the rate constants of decomposition and activation energies for the oxidative pyrolysis of Sample A and IPP. Table 4 compares the results of LOI studies for Samples B, D, E, and neat IPP.

Table 3

Kinetic Results of Oxidative Pyrolysis of Sample A and IPP

	Rate Constants, sec^{-1}		
Temp, °C	IPP(air)	Sample A(air)	Sample A(O_2)
240	2.5×10^{-3}	--	1.5×10^{-4}
264	5.4×10^{-3}	1.8×10^{-4}	3.9×10^{-4}
289	9.2×10^{-3}	3.4×10^{-4}	1.4×10^{-3}
313	--	1.2×10^{-3}	--
338	--	3.2×10^{-3}	--
Activation Energy, Kcal $mole^{-1}$	16	26	26

Table 4

LOI of Samples B, D, E, and IPP

Sample	LOI
B	26.4
D	18.3
E	17.7
IPP	17.4

The variation of LOI with respect to the concentration of chromium in each sample is shown in Figure 23. In this Figure, the LOI of each sample is plotted versus the weight percent of chromium in the sample. Finally, Table 5 shows the results of the elemental analysis of the residual char left after burning Sample B in air.

Table 5

Elemental Analysis of Char from Burning Sample B in Air

Elements	Weight Percent
Cr	0.9
Cl	0.17
C	80.51
H	9.52

Discussion of Results

There have been a lot of studies on the inhibition of the thermoxidative degradation of polypropylene by metal-containing compounds.

Osawa et al.[10] examined the effect of Zn, Cr, Co, Ni and Cu Se-carbamates on the thermoxidative degradation of IPP at 120°C, both in the presence and absence of copper stearate as oxidation accelerator. They concluded that these metal compounds are all effective inhibitors, even in the presence of copper stearate. On the other hand, the fatty acid salts of Co, Mn, Cu, Fe, V, Ni, Ti, Al, Mg, and Ba had been shown to catalyze the thermoxidative degradation of IPP at 125°C[6].

Bulewicz and Padley[17,18] and Matsuda and Gutman[19] indicated that the elements Mg, Cr, Mn, Sn, U, and Ba had pronounced effect on the recombination of H atoms and hence should be effective flame inhibitors. Hastie[20] reported the relative effectiveness of different inhibitors for n-hexane/air flame and chromyl chloride was one of the most effective ones.

Etard[14] discovered the reaction of chromyl chloride with hydrocarbons to form complexes and the mechanism was discussed by Necsoin et al.[21]. The selectivity of chromyl chloride towards the various types of carbon hydrogen bonds is not well understood.

Wiberg and Eisenthal[22] had shown that chromyl acetate is a reasonable model for chromyl chloride. In the reaction of low molecular weight hydrocarbons with the latter compound, Foster and Hickinbottom[23] had shown that the tertiary/secondary reactivity factor was 5. The corresponding factor for chromic acid reaction was more than 60.

The low degree of discriminacy reaction of chromyl chloride with ethylene-propylene copolymer had been reported by Burgert[24]. Therefore, it can be deduced that the reaction of chromyl chloride with polypropylene is probably random although the attack on the tertiary positions is still favored.

Samples A, B, and C consisted of different concentrations of Cr and Cl as a result of different experimental conditions. The reaction of chromyl chloride with polypropylene is quantitative if sufficient swelling and stirring of the polymer are allowed. For example, quantitative yield of Cr and Cl was obtained in Sample C with sufficient swelling and stirring of the sample before and after the reaction.

In inert atmosphere, Sample A decomposed faster than IPP and exhibited a lower activation energy of pyrolysis. In nitrogen, IPP was stable up to 300°C (with only 2 percent weight loss) while Sample A had a 14 percent weight loss. By comparison, Sample A decomposed faster than IPP at 388° and 414° but more slowly at 438°C. The presence of chromium accelerated the formations of methane, isobutylene, and $C_{10}H_{20}$ at 438°C, while at the same time, inhibited the formations of other products.

The DTA of Sample C and IPP in nitrogen were very similar to each other. Endothermic melting peaks appeared at about 150° and 163°C respectively for Sample C and IPP. The corresponding decomposition endotherms were at 465° and 450°C. Comparing the thermal stabilities of Sample A and Sample C (Figures 2 and 8) in nitrogen, these two samples were found to be very similar. The temperature for 50 percent weight loss of these two samples was about 400°C, the corresponding temperature for IPP was 390°C. Therefore, it is apparent that in inert atmosphere, chromium contributes little, if any, to the thermal stability of polypropylene.

The situation, however, was quite different in oxidative environment. The pyrolysis of Sample A in air was greatly inhibited. Sample A retained most of its weight at about 350°C while IPP was completely pyrolyzed at this temperature. At about 450°C, Sample A experienced a rapid weight loss and this was due to the ignition of the sample as was evidenced by the nose-effect on the TGA curve. Under this condition, the temperatures for 50 percent weight loss were about 415° and 325°C respectively for Sample A and IPP.

A 5 percent char was formed after the pyrolysis of Sample A. Presumably, oxygen oxidized the chromium to Cr_2O_3 which is a well known

catalyst for dehydrogenation of hydrocarbons in petroleum refining[25]. The activation energy for the pyrolysis of Sample A in air was 26 Kcal mole^{-1} and this is to be compared with just 16 Kcal mole^{-1} for IPP under similar conditions.

The inhibitive effect of chromium on the oxidative pyrolysis of polypropylene was also evidenced by the suppression of all of the major products in the temperature range from 240°-289°C. In addition, the inhibitive effect was greater the higher the temperature. For example, the total volatiles (up to C_6 oxygenates and C_7 hydrocarbons) from Sample A decreased from 64 percent to 42 percent of those from IPP when the temperature was increased from 240° to 289°C.

DTA in air at 60 ml min^{-1} had shown two strong exotherms occurring at about 400° and 250°C respectively for Sample C and IPP. This indicated that the self-ignition temperature of Sample C was increased relatively by 150°C with the presence of chromium in the polymer.

In pure oxygen at a flow rate of 25 ml min^{-1}, Sample A ignited at about 360°C, the corresponding ignition of IPP occurred at about 240°C. An increase in oxygen concentration (20 to 100 percent) in the pyrolysis of Sample A increased the rates of decomposition of the polymer but not the activation energy which remained the same for air and oxygen pyrolysis.

The char formed after burning Sample B consisted of 0.9 percent and 0.17 percent by weight of Cr and Cl. This showed that about 40 percent of Cr and 84 percent of Cl in the original sample had been consumed in the flame. The role of Cr and Cl is probably that of free radical trapping in the vapor phase. Chromium probably formed stable oxides which fumes served to blanket the flame and cut off oxygen supply to the flame

front[26]. The action of Cl, is probably that of flame 'poisoning' due to the formation of HCl[27]. The resistance of Sample A in burning was reflected by a LOI value of 26.4.

Conclusion

Chromyl chloride(CrO_2Cl_2) had been used to react with semi-crystalline IPP(Etard reaction) under different experimental conditions. The chromium-containing polymers were investigated for their thermal stabilities and ignition characteristics in inert and in oxidative atmospheres by TGA and DTA respectively.

Pyrolysis, oxidative pyrolysis, and limiting oxygen index(LOI) studies were performed on these polymers. Pyrolytic products and their distributions were also examined. The pyrolysis processes followed first-order reaction kinetics. Data obtained for neat IPP under similar conditions were used for comparison for all of the above studies.

Compared to polypropylene, the pyrolysis of chromium-containing polypropylene in inert atmosphere exhibited a lower activation energy. The opposite was true in oxidative environment where chromium formed in-situ char and inhibited pyrolysis. The self-ignition temperature of the chromium-containing polymer in air was also increased relatively by 150°C when compared to IPP.

The inhibitive effect of chromium on the oxidative pyrolysis of polypropylene was greater the higher the pyrolysis temperature studied. The total volatiles from a sample consisting of 2.22 percent by weight of chromium decreased from 64 percent to 42 percent of those from IPP when the temperature was increased from 240° to 289°C.

The sample that consisted of 1.5 percent Cr and 0.98 percent Cl acquired a LOI of 26.4. In burning this sample, almost half of the Cr and all of the Cl were consumed in the flame. It is believed that the action of Cr and Cl is that of free radical scavenging to form stable compounds, thus stopping flame propagation.

Acknowledgment

The author would like to thank the Borg Warner Chemical Company for their help in the limiting oxygen index test.

References

1. Moiseev, V.D., Neiman, M.B., Kriukova, A.I., Vysokmol. Soedin., 1, 1552, 1959

2. Straus, S., Wall, L.A., J. of Res. NBS, 65A, 3, 221, 1961

3. Chien, J.C.W., Boss, C.R., J. Polymer Sci., A-1, 5, 1683, 1967

4. Platza, N.A.J., ed., 'Stabilization of Polymers and Stabilizer Processes', 85, Advances in Chemistry Series, ACS, 1968

5. Abu-Isa, I., J. of Polymer Sci., A-1, 8, 961, 1970

6. Osawa, Z., Shibamiya, T., Matsuzaki, K., Kogyo Kagaku Zassbi, 71, 552, 1968

7. Khinkis, S.S., Frolova, N.B., Emelyanova, A.T., Borodulina, M.Z. Polyakov, Yu., N, Soviet Plastics, No. 7, 20, 1972

8. Lebedrva, L.P., Medvedeva, A.I., Gorodetskaya, N.N., Romanchenko, T. S., Mikherilov, V.V., Levin, P.I., Temchin, Yu., M., Soviet Plastics, No. 11, 64, 1972

9. Mamedov, R.I., Sadykhzode, S.I., Sultanov, R.A., Aliev, GD., Ali-Zade, E.M., Fataliev, A.G., Soviet Plastics, No. 6, 71, 1973

10. Osawa, Z., Ishizuka, T., Ogiwara, Y., Suzuki, H., Ishikawa, H., J. App. Polymer Sci., 16, 955, 1972

11. British Pat. 897,795 (May 30, 1962); Chemical Abstracts, 57, 8737C, 1962

12. Schurdak, E.J., Susi, P.V., Plastics Engineering, 32, August, 1978

13. Lenz, R.W., 'Organic Chemistry of High Polymers', 297, Interscience, N.Y., 1967

14. Etard, A., Ann. Chim. Phys., (5), 22, 218, 1881

15. Makhija, P.C., Stairs, R.A., Canadian J. of Chemistry, 46, 1255, 1968

16. Dietz, W.A., J. Gas Chromato., 68, 1967

17. Bulewicz, E.M., Padley, P.J., Proc. Roy. Soc., A323, 377, 1971

18. Bulewicz, E.M., Padley, P.J., 13th International Sym. on Combustion, Combustion Institute, 73, 1970

19. Matsuda, S., Gutman, D., J. Phys. Chem., 75, 2402, 1971

20. Hastie, J.W., J. of Res. NBS, 77A, 733, 1973

21. Necsoin, I., Balaban, A.T., Pascaru, I., Sliam, E., Elian, M., Nenitzescu, C.D., Tetrahedron, 19, 1133, 1963

22. Wiberg, K.B., Eisenthal, R., Tetrahedron, 20, 1151, 1964

23. Foster, G., Hickinbottom, W.J., J. Chem. Soc., 680, 1960

24. Burgert, B.E., J. Polymer Sci., C. No. 24, 233, 1968

25. Shreve, R.N., 'The Chemical Process Industries', 844, McGraw-Hill, N.Y., 1956

26. Hung, N.X., MS Thesis, University of Mass., 1975

27. Kuryla, W.C., Papa, A.J., ed., 'Flame Retardancy of Polymeric Materials', 2, 105, Marcel Dekker, N.Y., 1973

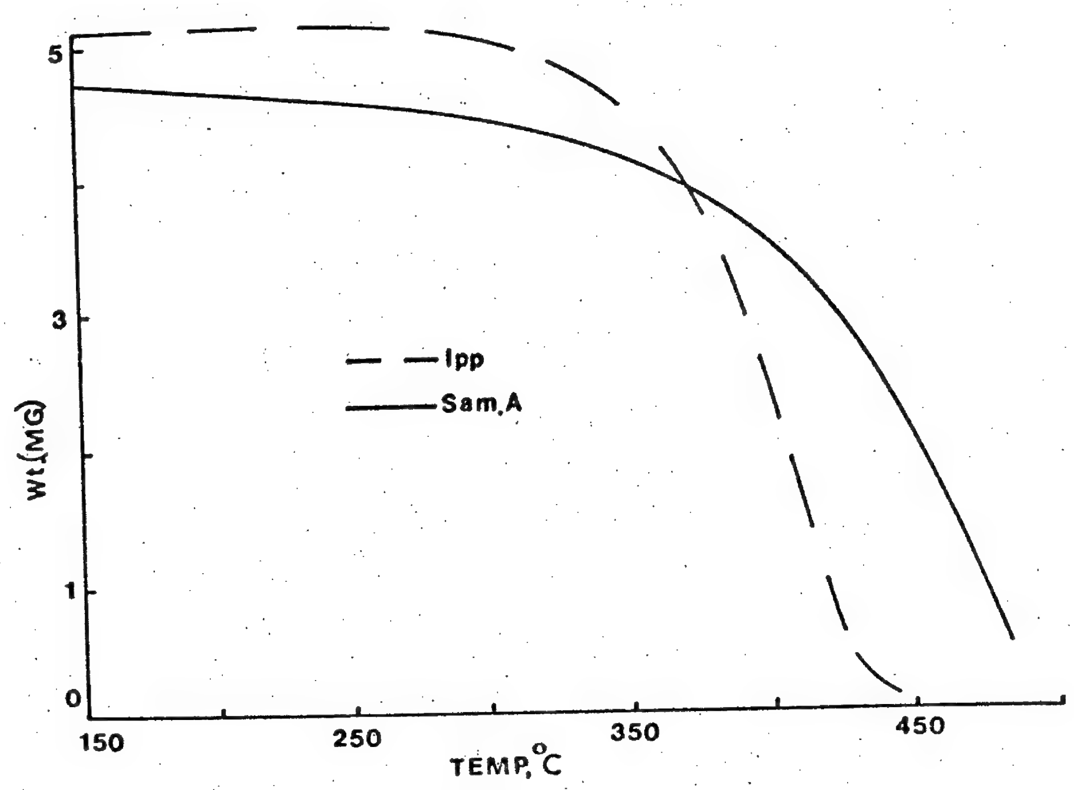


Fig. 1 TGA thermograms of Sample A and IPP in nitrogen

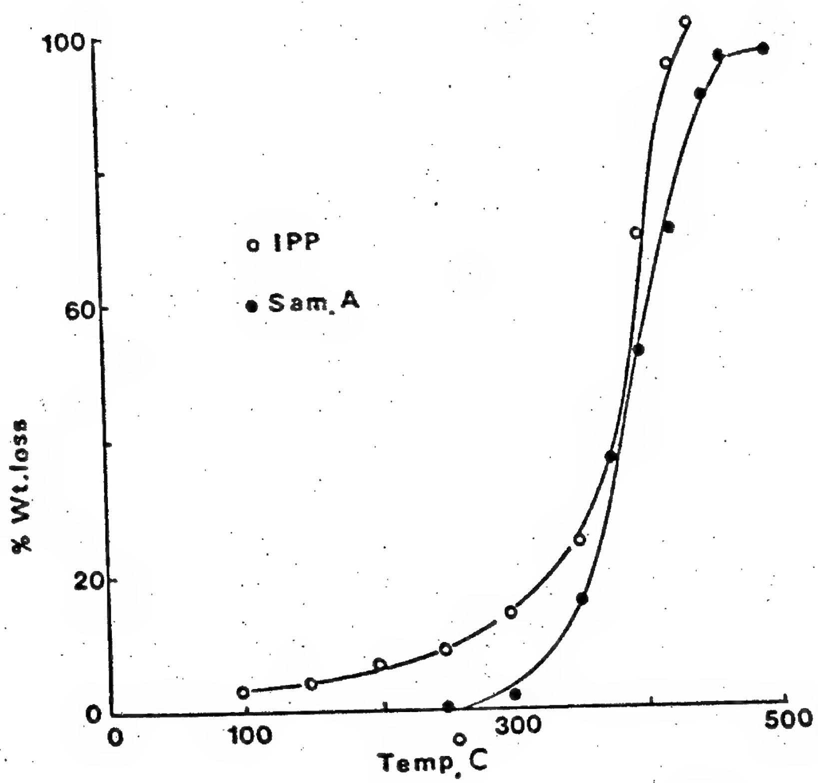


Fig. 2 Percent weight loss of Sample A and IPP in nitrogen as a function of temperature

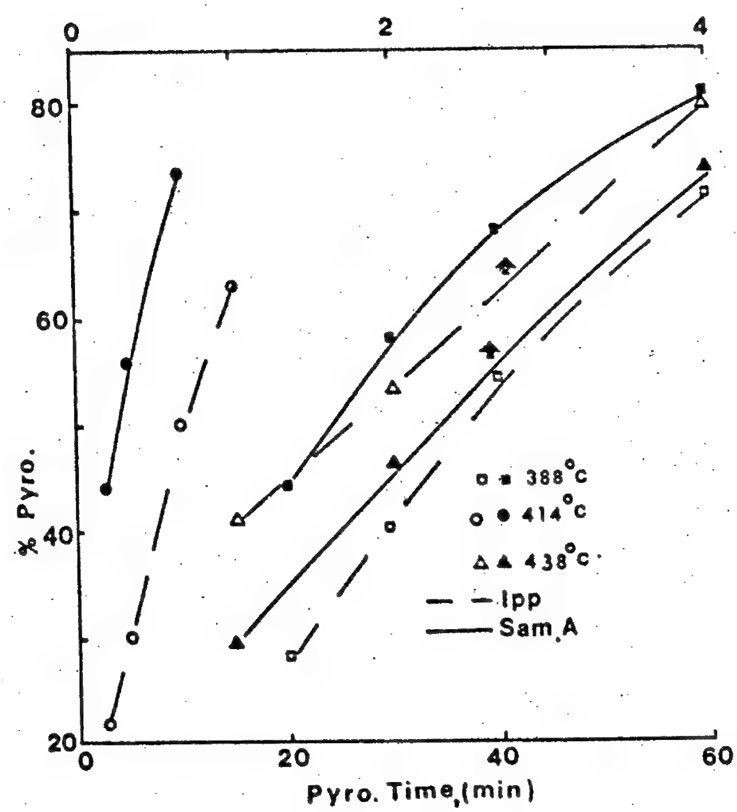


Fig. 3 Rates of pyrolysis of Sample A and IPP in helium at indicated temperatures

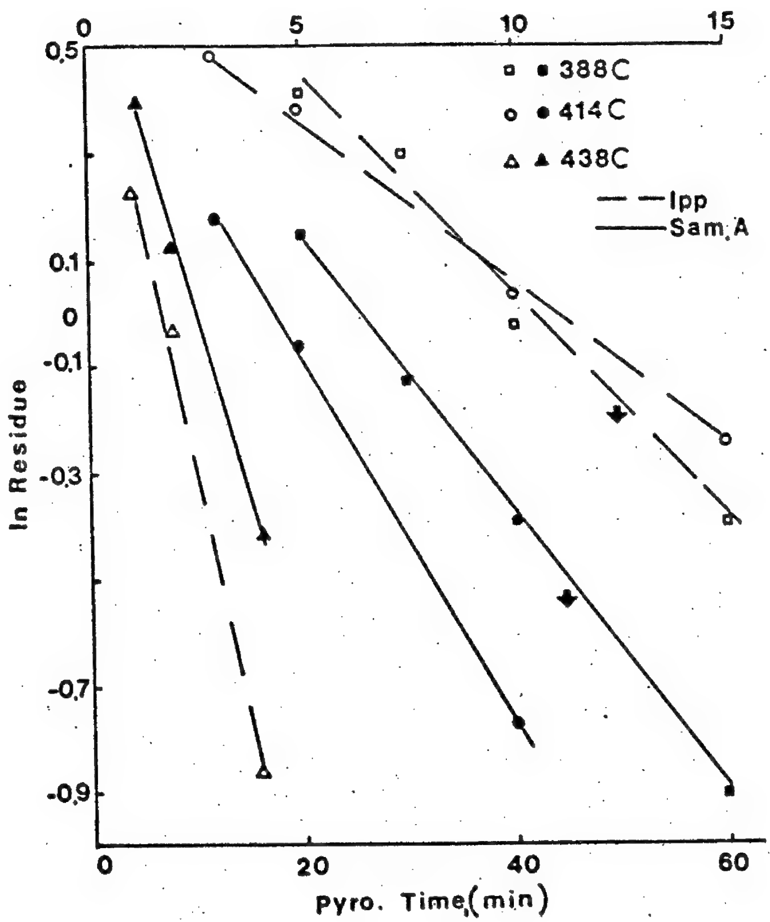


Fig. 4 First-order kinetic semilog plot of pyrolysis of Sample A and IPP in helium at indicated temperatures

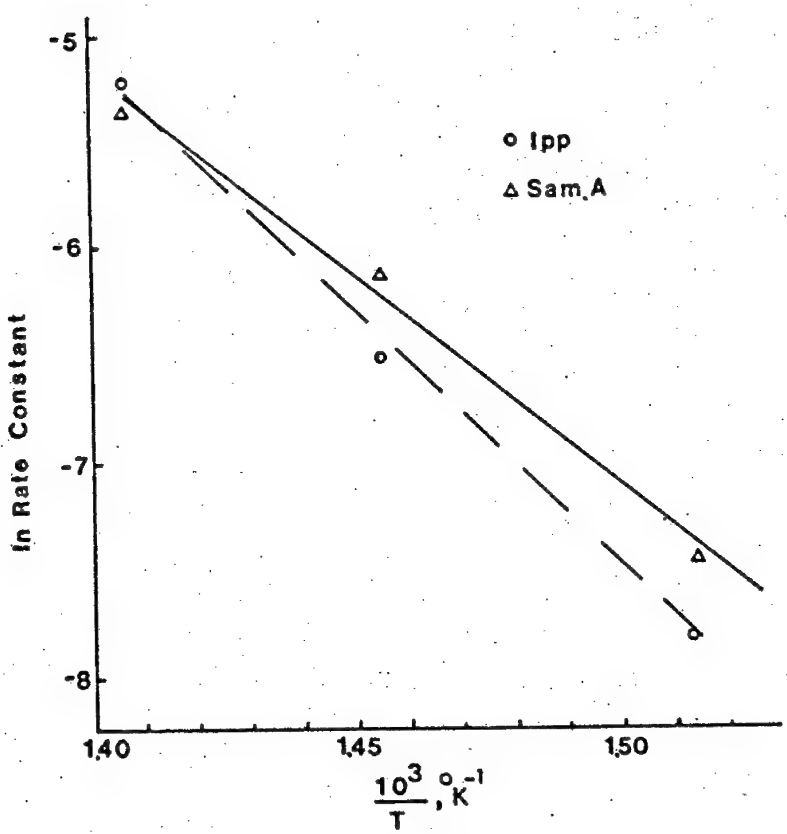


Fig. 5 Arrhenius plot for pyrolysis of Sample A and IPP in helium

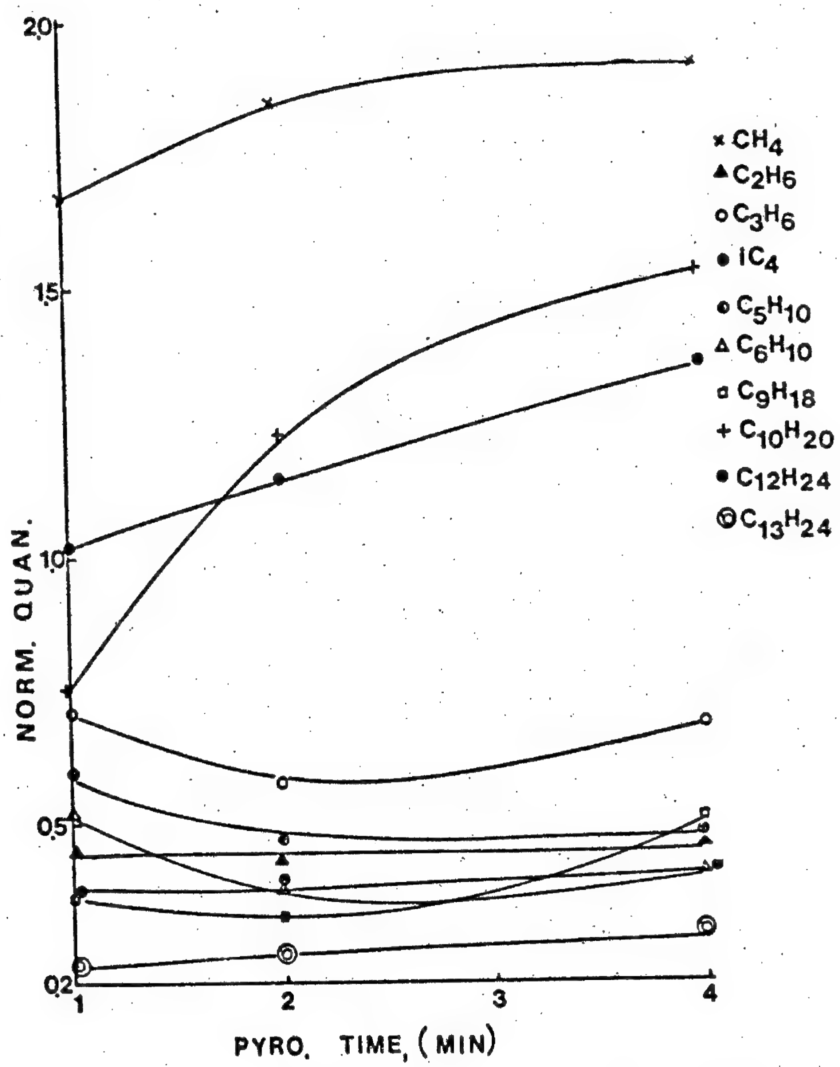


Fig. 6 Absolute normalized product distributions of pyrolysis of Sample A and IPP in helium at 438°C as a function of pyrolysis time

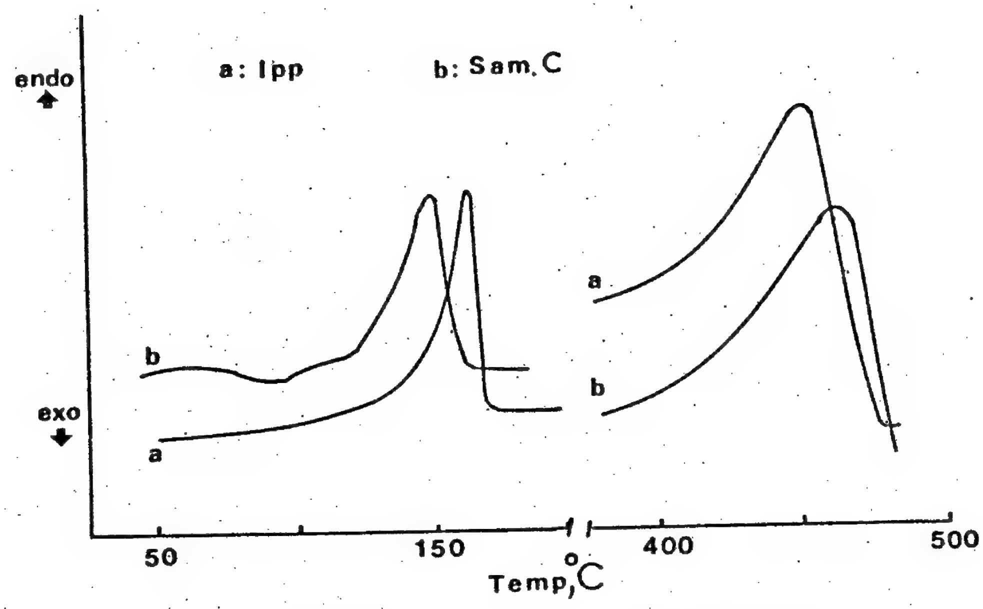


Fig. 7 DTA thermograms of Sample C and IPP in nitrogen

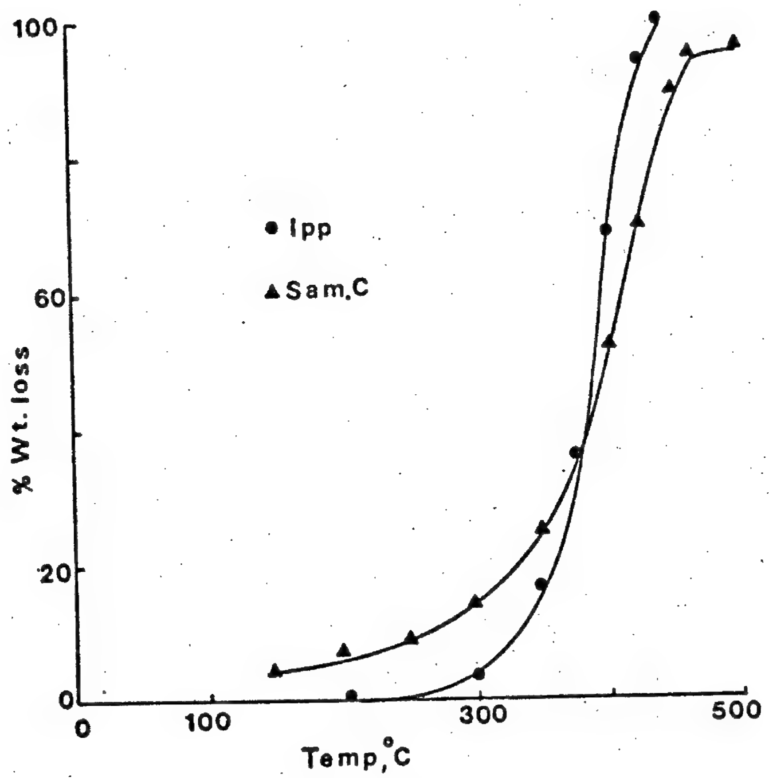


Fig. 8 Percent weight loss of Sample C and IPP in nitrogen as a function of tmperature

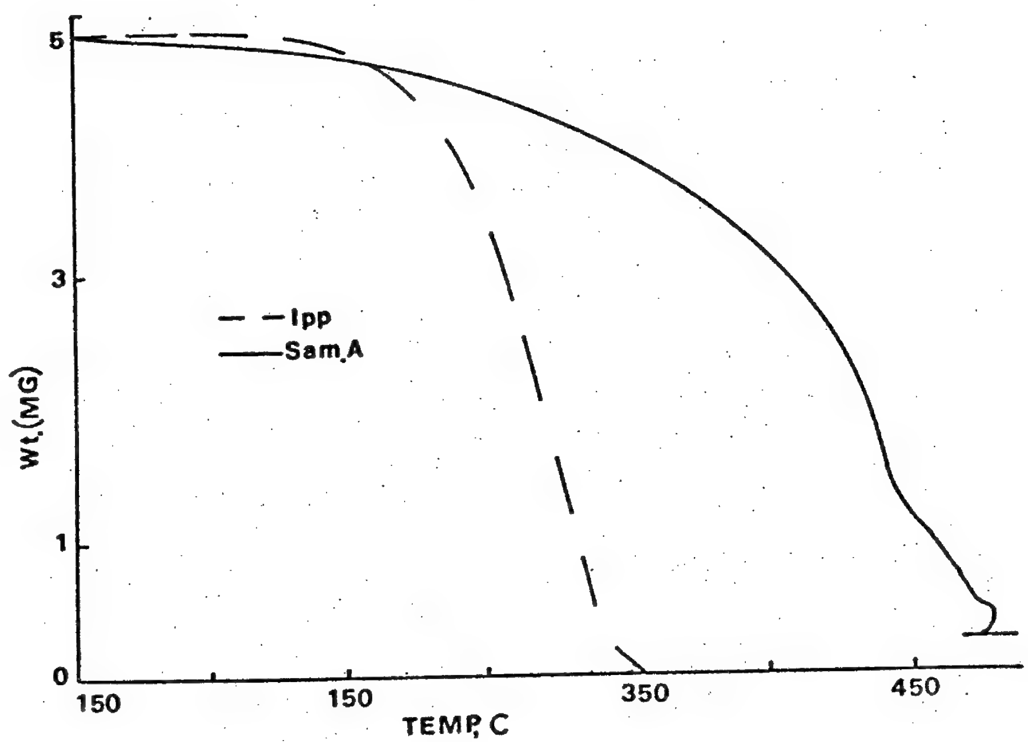


Fig. 9 TGA thermograms of Sample A and IPP in air

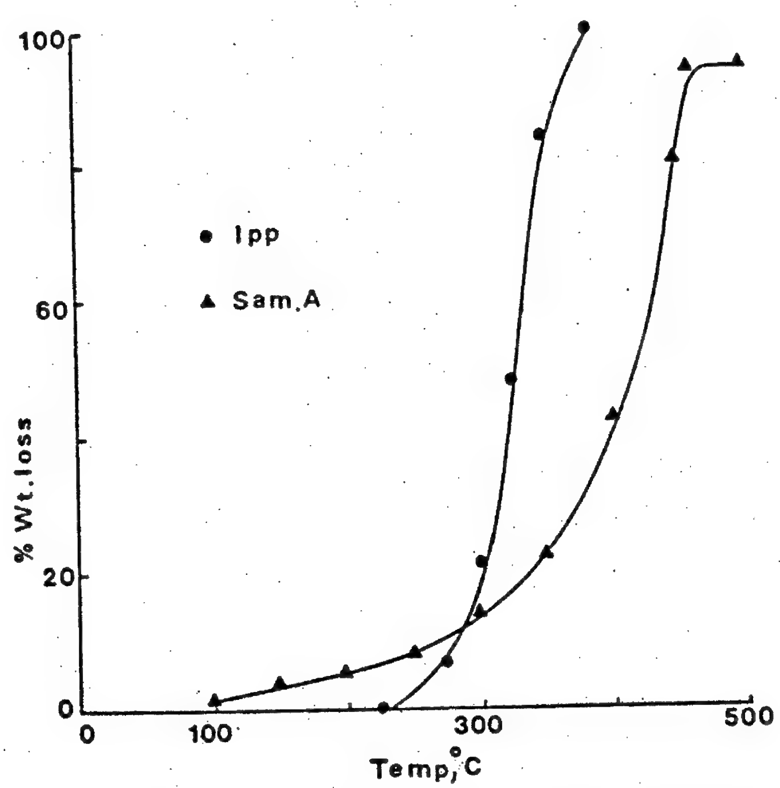


Fig. 10 Percent weight loss of Sample A and IPP in air as a function of temperature

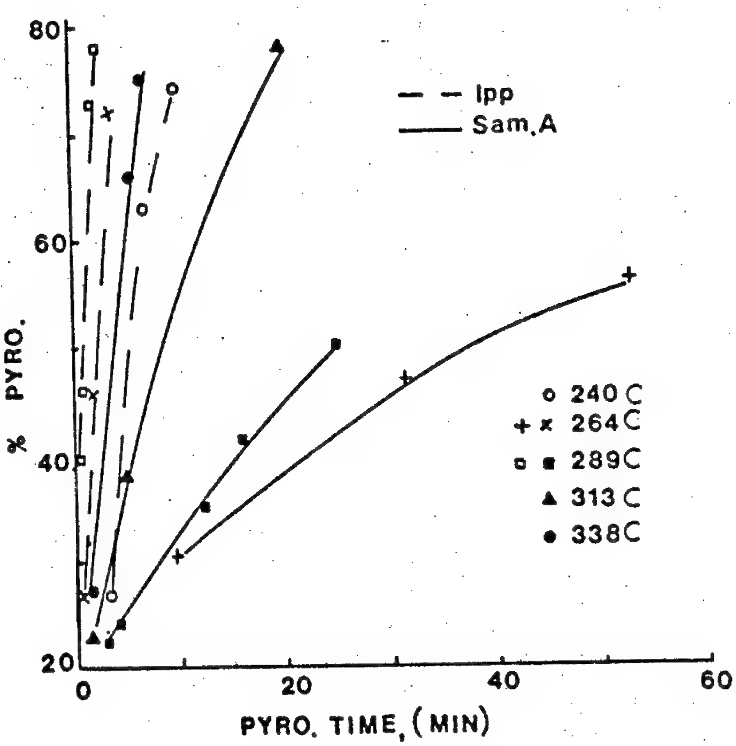


Fig. 11 Rates of pyrolysis of Sample A and IPP in air at indicated temperatures

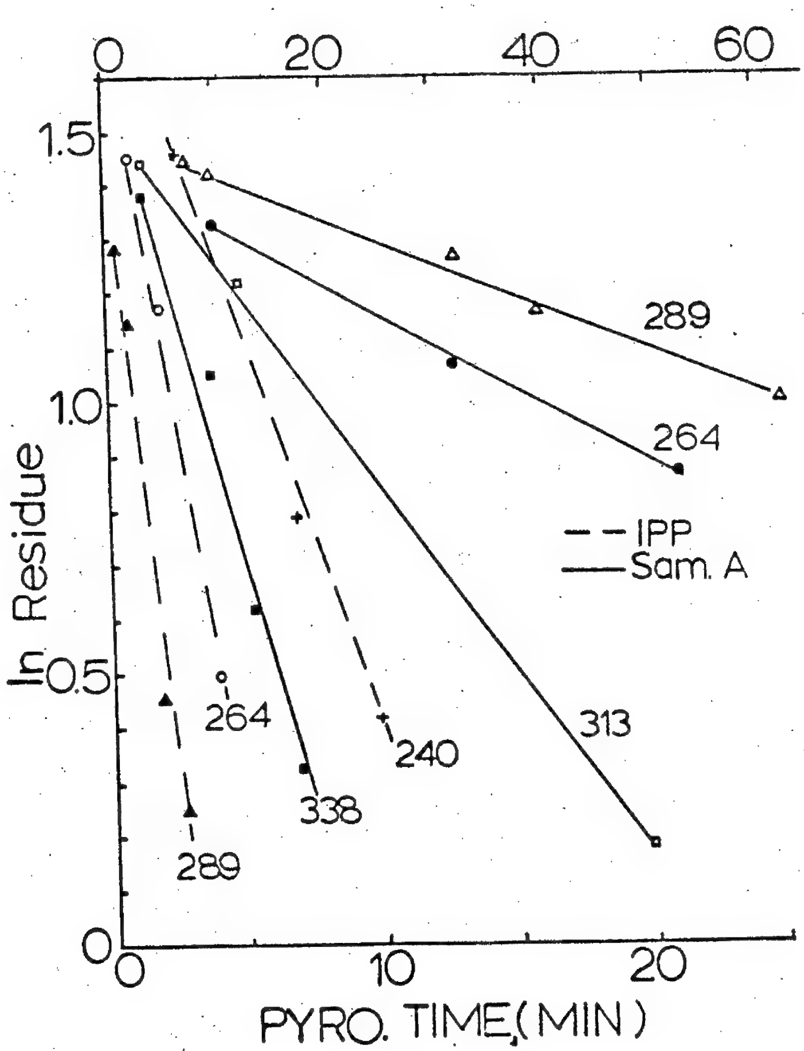


Fig. 12 First-order kinetic semilog plot of pyrolysis of Sample A and IPP in air at indicated temperatures

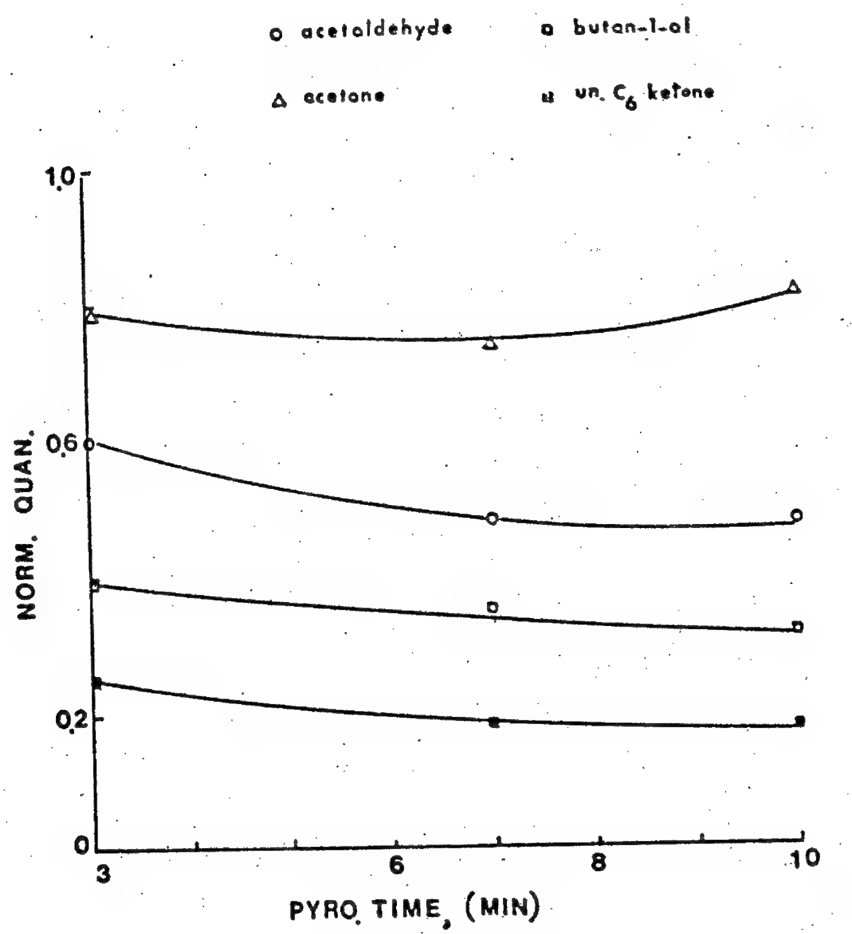


Fig. 13 Absolute normalized distributions of major products from pyrolysis of Sample A and IPP in air at 240°C as a function of pyrolysis time

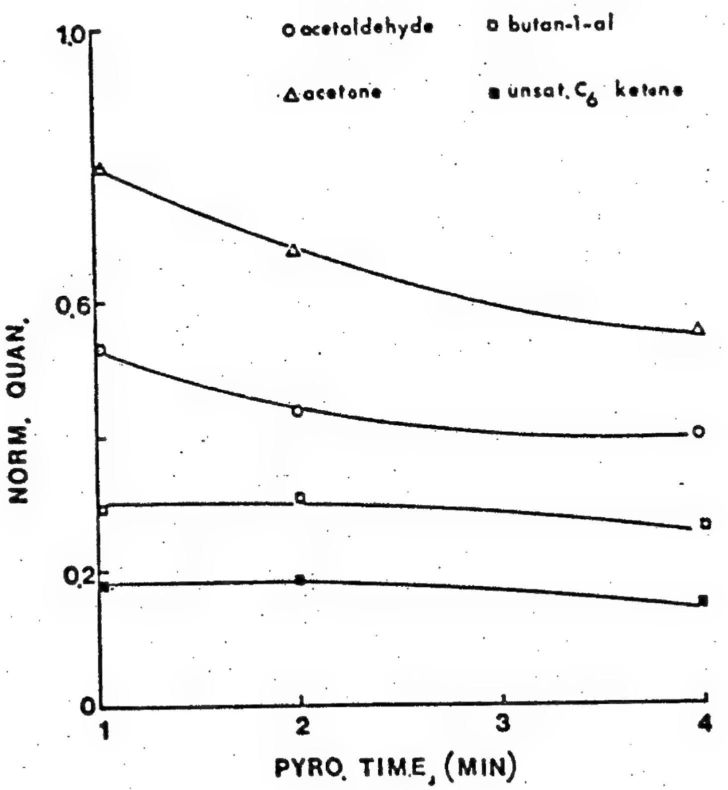


Fig. 14 Absolute normalized distributions of major products from pyrolysis of Sample A and IPP in air at 264°C as a function of pyrolysis time

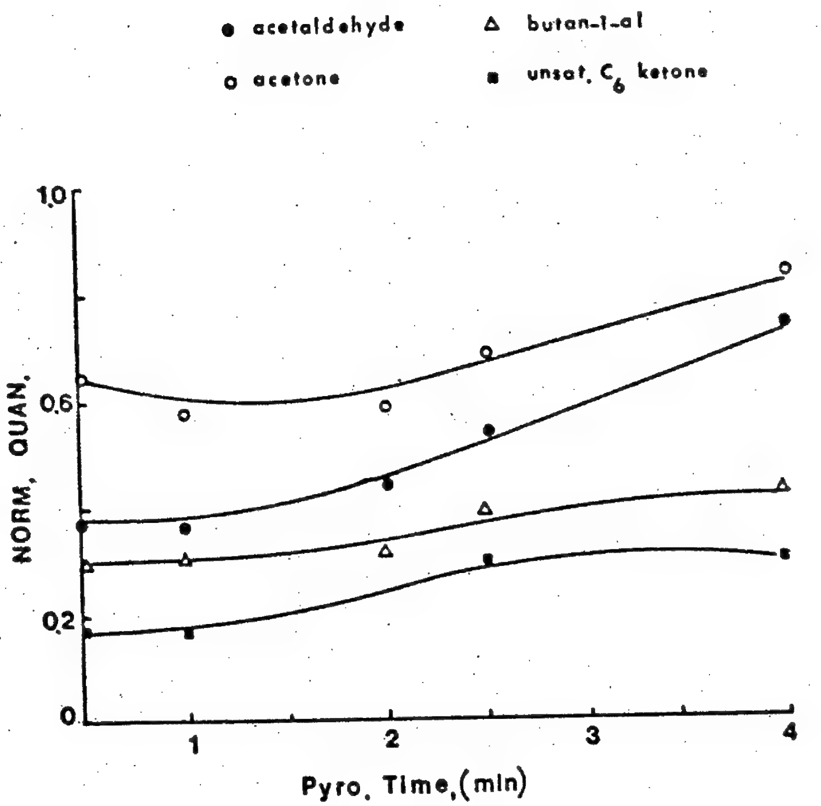


Fig. 15 Absolute normalized distributions of major products from pyrolysis of Sample A and IPP in air at 289°C as a function of pyrolysis time

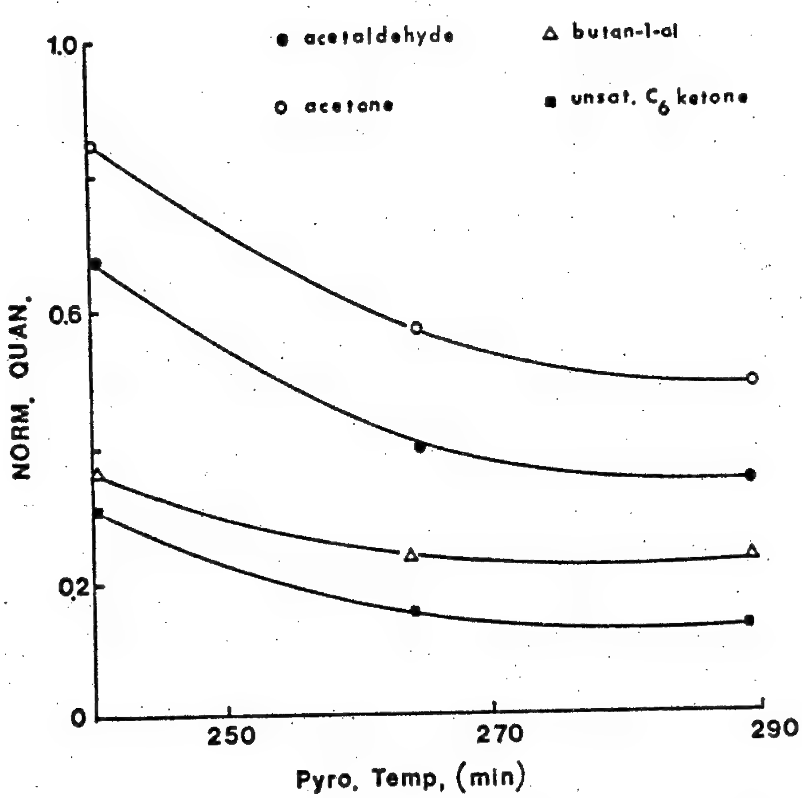


Fig. 16 Absolute normalized distributions of major products from pyrolysis of Sample A and IPP in air as a function of pyrolysis temperature

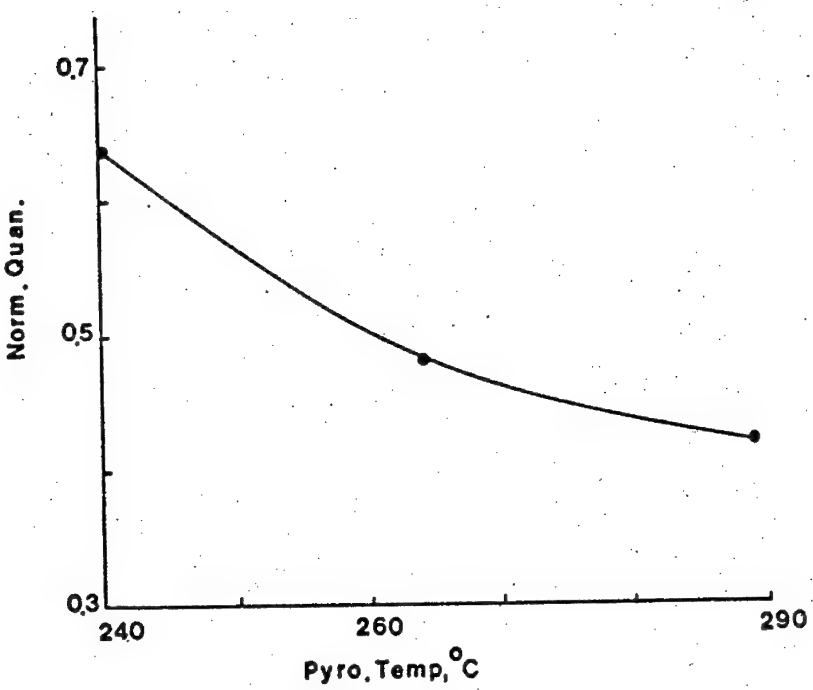


Fig. 17 Absolute normalized total volatiles of pyrolysis of Sample A and IPP in air as a function of pyrolysis time

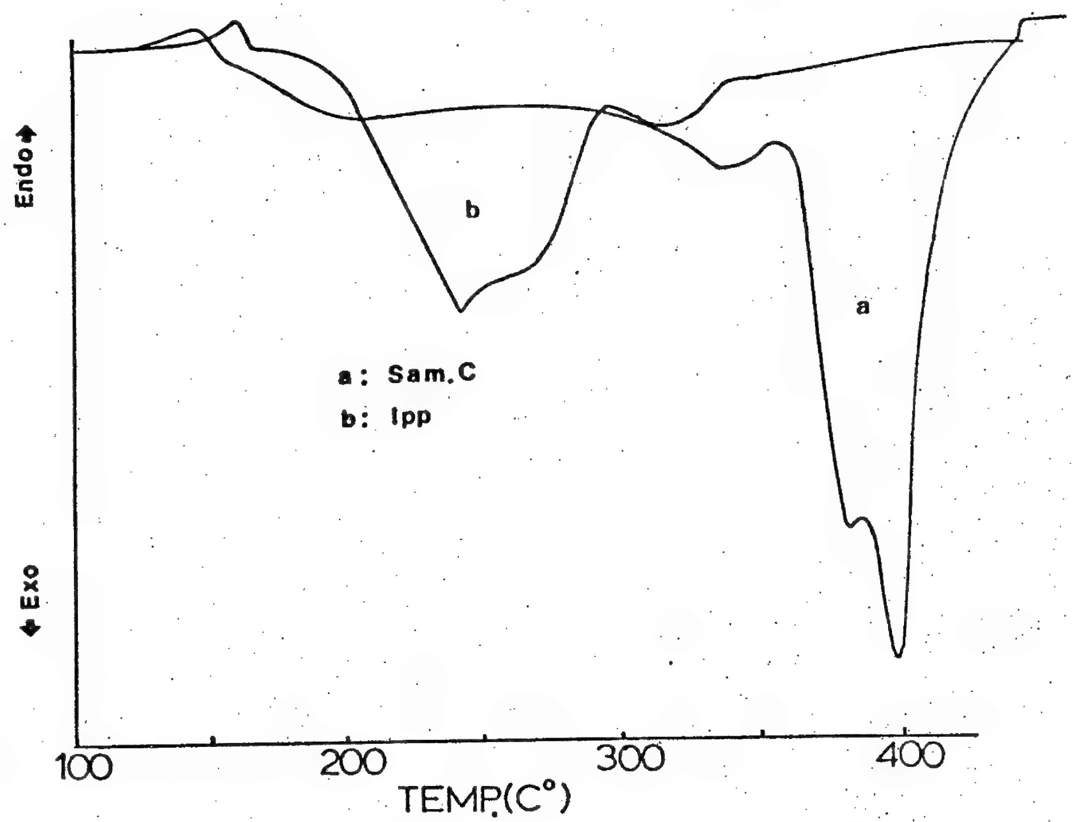


Fig. 18 DTA thermograms of Sample C and IPP in air

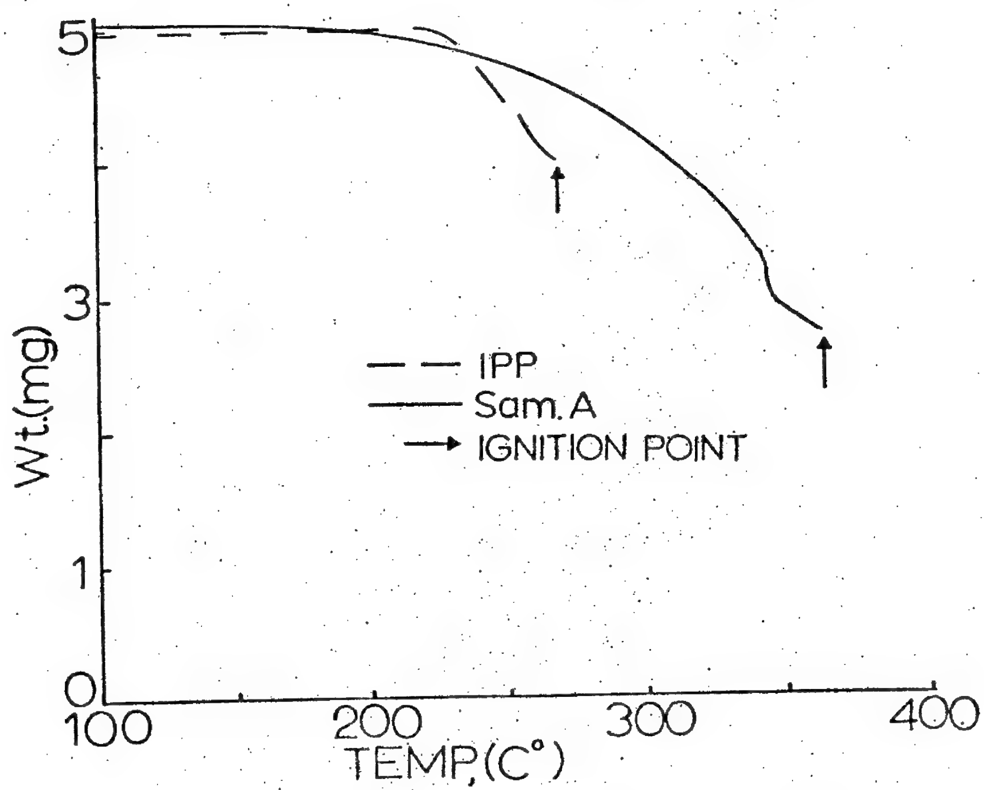


Fig. 19 TGA thermograms of Sample A and IPP in oxygen

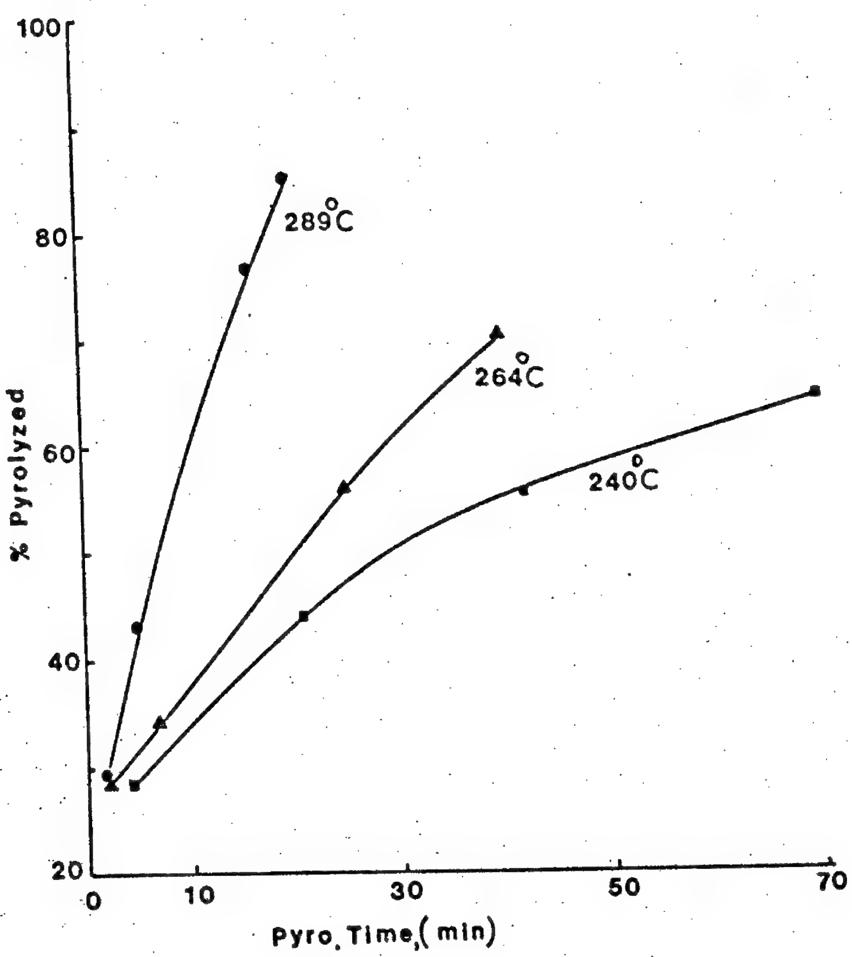


Fig. 20 Rates of pyrolysis of Sample A in oxygen at indicated temperatures

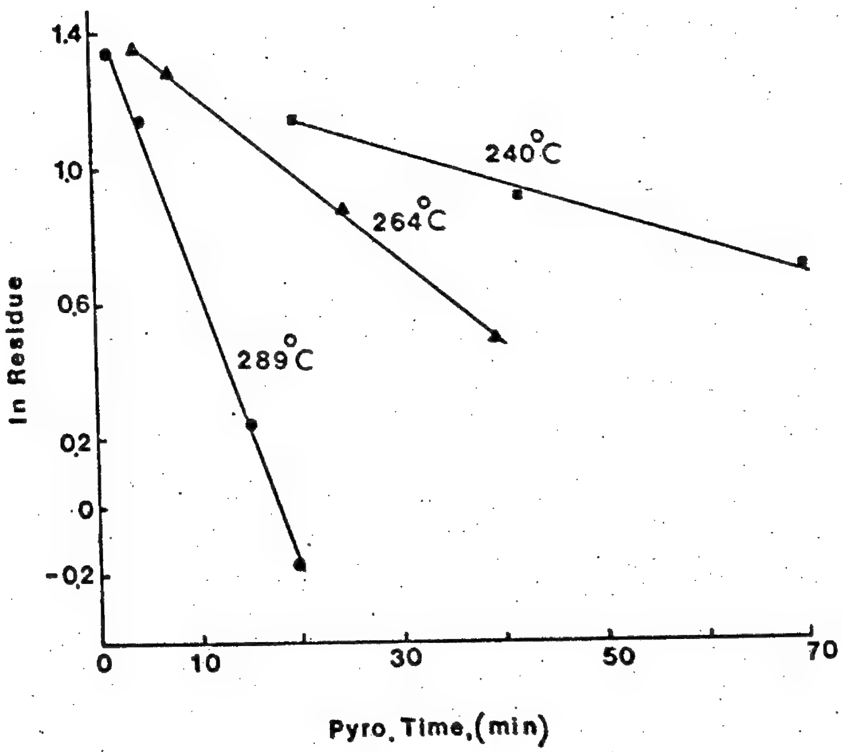


Fig. 21 First-order kinetic semilog plot pyrolysis of Sample A in oxygen at indicated temperatures

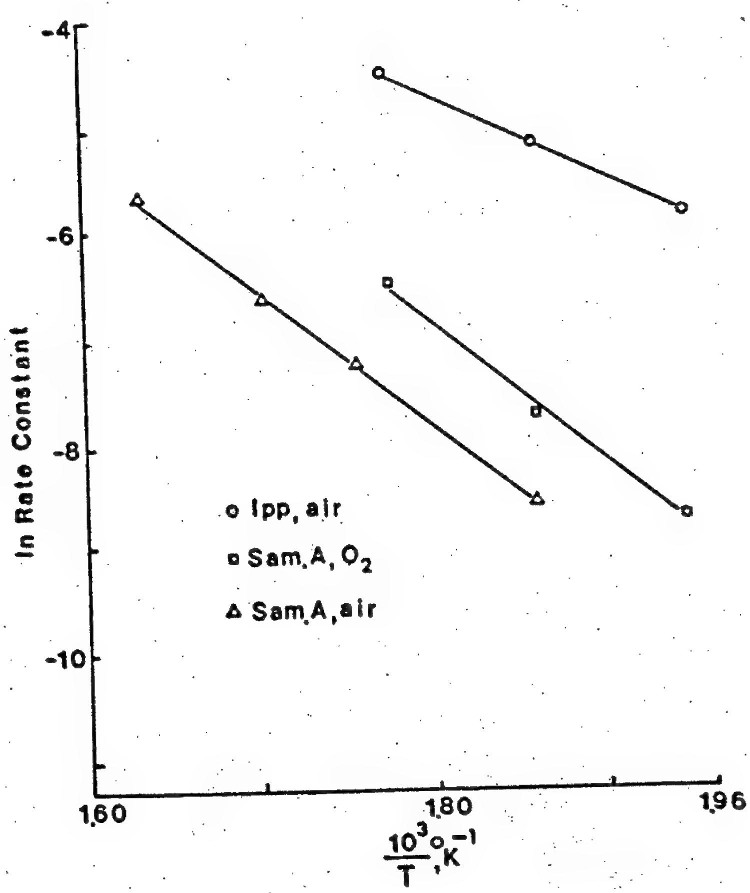


Fig. 22 Arrhenius plot for oxidative pyrolysis of Sample A and IPP

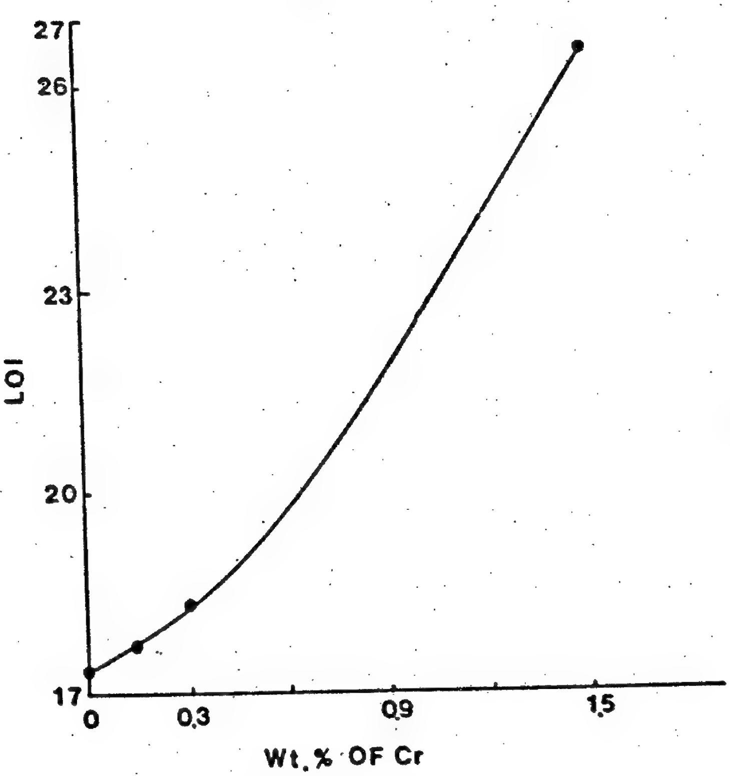


Fig. 23 Variation of LOI of Samples B,D, and E as a function of chromium concentration in each sample

CHAPTER VII

PYROLYSIS OF POLYISOPRENE

Abstract

Natsyn 2200 polyisoprene(PI) was pyrolyzed in helium from 315°-384°C. A novel interfaced gas chromatographic peak identification system(IPGCS) was used in the experiment. The products were separated by temperature programmed gas chromatography(GC) and analyzed by mass spectrometry(MS).

The pyrolysis of PI followed first-order reaction kinetics. The rates of decomposition at different temperatures were determined and an activation energy of 41 Kcal mole^{-1} was obtained for the process. The low activation energy was mainly due to the presence of 3,4 addition units in the polymer chain.

The major pyrolytic products were isoprene and dipentene. At 384°C, the two compounds occupied almost 90 percent by weight of the total volatiles. A simple mechanistic scheme was proposed which involved α and β scissions of the polymer chain to account for all of the products. Although products were formed from both types of scissions, β scissions, which led to the formation of allylic radicals, were mainly responsible for the formation of isoprene and dipentene.

Introduction

The history of destructive distillation of natural rubber goes back more than a century[1-5]. Later work by Madorsky, Straus and co-workers[6-8] involved pyrolytic fractionation in which the products were separated into fractions. The light fraction was analyzed by MS and the heavy fraction for its average molecular weight.

More recent study on the thermal behavior of rubber by pyrolysis-GC was reported by Jernejcic and Premru[9]. Retention time method was employed to identify the products. Pyrolysis-GC-MS was used by Galin-Vacherot[10] to study the pyrolysis products of PI in nitrogen. Hydrocarbons up to C_{10} were identified and the mechanism of product formations was briefly discussed.

In the present work, the pyrolysis of PI was performed with the IPGCS(see Chapter III) in helium. Pyrolytic products were separated by temperature programmed GC and identified on-the-fly by MS. The mechanisms of product formations were discussed. The kinetics of the pyrolysis process were also investigated. The results of this study were compared to other reported works.

Experimental

Natsyn 2200(Goodyear) PI consisting of about 97 percent cis 1,4 and 3 percent 3,4 units was used. The polymer contains a phenolic type antioxidant and has a number-average molecular weight of about 200,000[11]. To remove the antioxidant and other adulterants, the polymer was dissolved in toluene, precipitated with acetone and vacuum dried.

The pyrolysis temperatures were determined by TGA(DuPont 900 thermal analyzer) in nitrogen at a flow rate of 25 ml min^{-1} and a heating rate of 30°C min^{-1}. Pyrolysis experiments were conducted with the MP3 multi-purpose thermal analyzer. The conditions and the calibration of the above instrument were described in Chapter IV.

About 6 mg of sample was used in each pyrolysis experiment. The sample was loaded into the quartz tube and the latter was purged with helium for 4 minutes so as to get rid of residual air in the system. The oven was fist heated up to the pyrolysis temperature and was then quickly moved towards the portion of the tube that contained the sample. About 30 seconds were required for the oven to return to its original temperature. Pyrolyses were performed at 315°, 340°, 364° and 384°C respectively and for different periods of pyrolysis time. The weight of the residue after each pyrolysis was obtained with a microbalance.

Two columns were used to separate the pyrolysis products with flame ionization detection and temperature programming at 4°C min^{-1}. A Chromosorb 102 column (12 ft x 1/8" O.D.) was used for the low-boilers and a 4 percent SE30 on ABS column was employed for the high-boiling products.

The products were analyzed by MS in a similar manner as described in Chapter III (Experimental Techniques). The distributions of products at complete pyrolysis were studied at 384°C (10 min). The relative weight percent of each product was calculated from its area under peak, taking into consideration of the detector attenuation factor, and normalized with respect to the total volatiles.

The pyrolysis of PI in inert atmosphere followed first-order reaction kinetics. The rate constants of decomposition and the activation energy for the process were determined.

Results

Figure 1 shows the TGA curve of PI in nitrogen. Figures 2 and 3 show the low and high-boiling pyrograms obtained by the Chromosorb 102 and the SE30 columns respectively. The numbers followed by x signs represent the detector attenuation factors. The numbers adjacent to each peak refer to the peak numbers in Tables 1 and 2. Table 1 shows the low-boiling compounds and their corresponding MS fragmentation patterns. Table 2 shows the same for the high-boiling products. The underlined mass numbers represent the most abundant species. The relative weight percent of each product is calculated by the method according to Dietz[12] who has shown that for all practical purposes, the flame ionization detector is equally sensitive to all hydrocarbons.

Figures 4 and 5 show the rate of pyrolysis of PI in helium at indicated temperatures and the corresponding first-order kinetic semilog plot. Figure 6 shows the resulting Arrhenius plot for the process.

Finally, Table 3 summarizes the results of the kinetic studies of the pyrolysis of PI in helium.

Table 1

Distribution of Low-Boiling Products and MS Fragmentation Patterns of the Pyrolysis of PI in He at 384°C

Peak number	Product	Weight percent	Fragmentation pattern
1	Methane	0.04	16, 15, 14
2	Ethylene	0.08	28, 27 26
3	Ethane	0.03	30, 29, 28, 27, 26
4	Propylene	0.15	42, 41, 39, 27
5	Propane	0.06	44, 43, 29, 28, 27
6	Isobutylene	0.09	56, 41, 39
7	Butenes	0.07	
8	Methyl butene	0.09	70, 55, 42, 41, 39, 29, 27
9	Isoprene	29	68, 67, 53, 41, 40, 39, 27

Table 2

Distribution of High-Boiling Products and MS Fragmentation Patterns of the Pyrolysis of PI in He at 38[illegible]°C

Peak number	Product	Weight Percent	Fragmentation pattern
10	Toluene	0.02	92, 91, 65, 39
11	2,3DMCP[a]	1.2	96, 81, 79, 67, 55, 53, 41, 39, 27
12	Octene	0.05	112, 97, 55, 41, 27
13	2,4DMCH[b]	0.16	110, 95, 82, 67, 39
14	m-xylene	0.33	106, 91, 51, 39
15	1M4ECH[c]	0.18	124, 109, 81, 67, 53, 41, 27
16	1,5DM5VCH[d]	2.5	136, 121, 107, 93, 68, 53, 39
17	Dipentene	60	136, 119, 107, 93, 68, 67, 53, 41, 39, 27
18	$C_{11}H_{18}$	0.2	
19	$C_{12}H_{18}$	0.2	
20-23	$C_{15}H_{24}$	3.5	
24-26	$C_{16}H_{26}$	1.8	
unidentified		0.3	

[a]2,3 dimethyl cyclopentene

[b]2,4 dimethyl cyclohexene

[c]1-methyl-4-ethyl cyclohexene

[d]1,5 dimethyl-5-vinyl cyclohexene

Table 3

Kinetic Results of the Pyrolysis of PI in He

Temp, °C	Rate Constants, sec^{-1}
315	3.0×10^{-4}
340	1.3×10^{-3}
364	4.8×10^{-3}
384	1.1×10^{-2}
Activation Energy, Kcal $mole^{-1}$	41

Discussion of Results

There have been a lot of studies published on the pyrolysis of PI. Different products were reported depending on experimental conditions, procedures, apparatus, sample, and sample size employed. Despite these differences, all studies have indicated that in the pyrolysis of PI, the main products are the monomer and its dimer, dipentene(1 methyl-4-isopropenyl cyclohexene).

Midgley and Henne[4] pyrolyzed natural rubber in bulk by destructive distillation at 700°C and identified C_5-C_{10} aliphatic and cyclic hydrocarbons. Madorsky et al.[13] pyrolyzed PI in vacuum from 302°-405°C and obtained 5.2 percent by weight of dipentene. No attempt was made to examine the light hydrocarbons.

Vacherot[10] pyrolyzed Hevea rubber (97 percent cis 1,4 and 3 percent 3,4 units) in nitrogen at 500°C and obtained C_1-C_{10} hydrocarbons. Basing on total volatiles, the yields of isoprene and dipentene were 66 percent

and 30 percent respectively. Other PI samples with different structures were also examined.

More recently, Van De Weil and Tommassen[14] studied the pyrolysis of Natsyn 200 PI at 620°C in a flowing stream of nitrogen and again identified C_1-C_{10} hydrocarbons. Basing on total volatiles, the yeilds of isoprene and dipentene were 19.5 percent and 6.4 percent.

In the present study, pyrolysis of PI was performed from 315°-384°C in a flowing stream of helium. Products from C_1-C_{16} hydrocarbons were identified by MS. At 384°C (10 min), complete pyrolysis of the polymer yielded 29 percent by weight of isoprene and 60 percent by weight of dipentene.

Vacherot[15] had shown that the ratio of dipentene to isoprene obtained in the pyrolysis of PI decreased with increase in pyrolysis temperatures and was independent of the molecular weight of the polymer. The ratio of dipentene to isoprene was about 2 in the present work and an average ratio of about 1 was found by Madorsky et al.[13] between 302°-405°C. Vacherot and Marchal[15] obtained ratios of 0.45, 0.35, and 0.15 respectively at 500°, 600°, and 800°C. The value at 600°C could be compared with 0.33 as reported by Van De Weil and Tommassen[14] at 620°C. On the other hand, Hulot and Lebel[16] had shown that at 700°C, the pyrolysis of PI gave essentially the monomer. The conclusion that can be drawn from the above is that at high temperatures, isoprene is formed at the expense of its dimer.

When the products in this work are compared to the above cited studies[4,10,13,14], only three products are in common. They are butenes, isoprene, and dipentene. C_1-C_3 hydrocarbons were identified in the two more recent studies[10,14] but were not reported in the two earlier works[4,13].

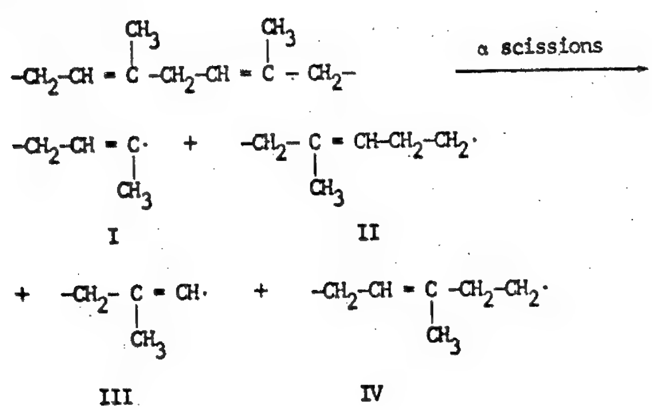
These hydrocarbons are believed to be present, but owing to perhaps experimental difficulties at that time, the earlier workers were unable to identify them.

The results by Vacherot[10] compares most favorably with this work. Eleven out of 16 products found by this worker are in common with the present study. Methyl cyclohexene was found by Vacherot[10] and Midgley[4], this work identified its isomer, 2,3 dimethyl cyclopentene instead.

Midgley[4] identified p-methyl-ethyl benzene, a probable secondary product of 1 methyl-4-ethyl cyclohexene found in this work. Benzene was reported by Madorsky[13], Van De Weil[14] and Midgley[4] but not in this work. Banerjee et al.[17] pyrolyzed Hevea rubber at 900 C° and found significant amounts of benzene, toluene, and m-xylene. Secondary reactions were proposed for their formations.

In order to reconcile to some extent the above cited results, a discussion of the mechanisms of the pyrolysis of PI is necessary. To account for the formations of isoprene and dipentene, the following mechanisms are proposed.

<u>Chain Initiation</u>



(1)

$$\xrightarrow{\beta\ \text{scissions}} \underset{\text{V}}{-CH_2-CH=\underset{\substack{|\\ CH_3}}{C}-CH_2\cdot} \quad + \quad \underset{\text{VI}}{-CH_2-\underset{\substack{|\\ CH_3}}{C}=CH-CH_2\cdot}$$

where I and III are vinyl radicals, II and IV are alkenyl radicals, and V and VI are allylic radicals.

Unzipping

Isoprene monomer can be formed from scissions accompanied by 1,3 and 2,4 hydrogen transfers involving III and IV respectively and also from V and VI with no hydrogen transfer.

$$\text{III or IV} \longrightarrow \text{III}' \text{ or IV}' + \text{isoprene} \qquad (2)$$

$$\text{V or VI} \longrightarrow \text{V}' \text{ or VI}' + \text{isoprene} \qquad (3)$$

Unzipping is more important in PI than in polypropylene. At 384°C, basing on total volatiles, the formation of isoprene was about 29 percent by weight while under similar conditions, the yield of propylene was about 10 percent. Unzipping in PI becomes even more important at high temperatures and for polypropylene, it is still not the dominant reaction.

Binder and Ransaw[18], and Hackathorn and Brock[19] showed that the main products of thermal dimerization in the pyrolysis of PI was diprene(1 methyl-5-isopropenyl cyclohexene). This work, however, found dipentene as the main dimerization product.

There are 18 possible dimers of isoprene and only 4 cyclohexene dimers have been produced in identifiable amounts in the pyrolysis of PI[20]. These 4 dimers are dipentene, diprene, 1,5 dimethyl-5-vinyl cyclohexene (1,5 DMVC), and 1,4 dimethyl-4-vinyl cyclohexene (1,4 DMVC). Without

considerating the presence of 1,2 units, the formation of these compounds are illustrated in the following Equations.

$$\left(CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_2 \right)_2 \longrightarrow \text{dipentene} + \text{1,5 dimethyl-5-vinyl cyclohexene} \qquad (4)$$

(1,4 - 1,4)

$$-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_2-CH_2-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_2- \longrightarrow \text{diprene} + \text{1,4 dimethyl-4-vinyl cyclohexene} \qquad (5)$$

(1,4 - 4,1)

$$-CH_2-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_2-CH_2-\underset{\displaystyle \overset{\displaystyle C-CH_3}{\underset{\displaystyle CH_2}{\|}}}{\underset{|}{CH}}- \longrightarrow \text{dipentene} + \text{1,5 dimethyl-5-vinyl cyclohexene} \qquad (6)$$

(4,1 - 4,3)

and

$$-\underset{\displaystyle \overset{\displaystyle C-CH_3}{\underset{\displaystyle CH_2}{\|}}}{\underset{|}{CH}}-CH_2-CH_2-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_2- \longrightarrow \text{diprene} \qquad (7)$$

(3,4 - 4,1)

It is apparent from the above illustrations that the dimers one obtains depend on the structure of PI used and any irregularities thereof. The sample employed in this work consists of 97 percent cis 1,4 and 3 percent 3,4 units, hence, all of the dimer products produced from Equations 4-7 need to be considered.

Since the presence of 3,4 units and structural irregularities are small, Equation 4, which describes the regular 1,4 units, is the major source of dimer products. This Equation also represents the formation of dipentene and 1,5 DMVC from the allylic radicals V and VI as shown in Equation 8.

$$\text{V or VI} \longrightarrow \text{V' or VI'} + \text{dipentene} + \begin{array}{c}\text{1,5 dimethyl-5-vinyl}\\ \text{cyclohexene}\end{array} \qquad (8)$$

The formation of the above two products is further enhanced by the presence of 3,4 units as shown in Equation 6. The presence of 3,4 units also leads to the formation of diprene(Equation 7) which is also formed together with 1,4 DMVC from head-head linkages of 1,4 units in Equation 5.

The allylic radicals V and VI are primarily responsible for the formation of dipentene as shown in Equation 8. These allylic radicals are formed by β scissions of the polymer chain as illustrated in Equation 1. However, Madorsky in his text[21] had reported that the α bonds, while weakened by being adjacent to a tertiary carbon are at the same time strengthened through the resonance from the double bond and as a result, the α bonds are generally weaker than the β bonds. It is believed that the resonance from the double bond is actually hyperconjugation (no bond resonance) and its contribution to resonance stablization is negligible. Results from this study has shown that β bonds are the weaker bonds as were also reported by Bolland et al.[21] and Jellinek[22].

Vacherot and Marchal[15] observed that the presence of 3,4 units in PI yielded an additional C_{10} hydrocarbon product and that the ratio of areas of this peak to that of dipentene varies linearly with the ratio

of 1,4 and 3,4 units. This hydrocarbon was later identified by Vacherot[10] to be 1,5 DMVC. Its yield was increased from 2 percent for Hevea rubber with 97 percent cis 1,4 and 3 percent 3,4 to 29 percent for a PI sample with 46 percent cis 1,4 and 56 percent 3,4 units.

In the above study, pyrolysis was performed in a stagnant nitrogen atmosphere and a Diels-Alder reaction involving a 3,4 unit and an isoprene monomer was proposed for its formation.

$$\begin{array}{l} -CH_2-CH_2- \\ \;\;| \\ \;\;C-CH_3 \\ \;\;\| \\ \;\;CH_2 \end{array} + \begin{array}{l} CH_2 = C-CH = CH_2 \\ \qquad\;\; | \\ \qquad\;\; CH_3 \end{array} \longrightarrow \begin{array}{l}\text{1,5 dimethyl-5-vinyl} \\ \text{cyclohexene}\end{array} \qquad (9)$$

It is apparent that the above secondary reaction depends, of course, on the close proximity of isoprene monomers. If the isoprene is not flushed away once it is formed, the above secondary reaction is highly probable. In the present study, secondary reactions were minimized by a sweeping atmosphere, thus the formation of 1,5 DMVC through 3,4 units in this manner (Equation 9) is less likely to occur.

Besides dipentene, only one C_{10} hydrocarbon has been identified in the present work and it has a molecular weight of 136 as determined by MS. This dimer is probably 1,5 DMVC formed together with dipentene from the allylic radicals V and VI (Equation 8). The presence of 3,4 units in the polymer chain further enhances its formation (Equation 6). However, two other dimers, diprene and 1,4 DMVC, formed from head-head linkages of 1,4 - 4,1 and 3,4 - 4,1 units (Equations 5 and 7) are also possible candidates.

Chain Propagation

The discussion of the mechanism of the pyrolysis of PI is traditionally based on the two major products, isoprene and dipentene. The author is not aware of any significant work that includes the discussion of the formations of minor products. These products can be formed as shown in the following Equations. The underlined compounds were those found in this work and compounds with dotted lines were also found but formed by secondary reactions. The numbers above the arrows indicate the modes of hydrogen transfer while those in brackets represent the positions of the carbon atoms at which transfer processes take place.

From the vinyl radical I

I $\xrightarrow{1,3}$ I' + 1,3 pentadiene

$\longrightarrow$ I' + 2,3 dimethyl cyclopentene + methyl cyclohexene
+ 1,3 dimethyl cyclohexadiene

$\longrightarrow$ I' + 1,4 dimethyl cyclohexene + propylene
+ 1,3 butadiene

$\longrightarrow$ I' + ethane + m-xylene + 1,3 pentadiene

$\longrightarrow$ I' + ethylene + 2 methyl-1-butene + m-xylene

$\longrightarrow$ IV' + 2 methyl-1-butene + m-xylene + acetylene
+ propylene

$\xrightarrow{1,2}$ V' + 1,2 butadiene

$\longrightarrow$ V' + 1,5 dimethyl vinyl cyclohexene
+ 1,5 dimethyl-5-vinyl cyclopentene
+ isoprene + 1,2 butadiene
+ 2-butene + pent-1-en-3 yne (10)

From the alkenyl radical II

II $\xrightarrow{1,2}$ II' + 1,3 pentadiene

$\longrightarrow$ II' + m-xylene + ethane

$\longrightarrow$ III' + ethylene

$\longrightarrow$ III' + methyl cyclohexene + 1,3 dimethyl cyclohexadiene
+ethylene + 2,3 dimethyl cyclopentene
+ 2-butene

$\longrightarrow$ III' + acetylene + propylene + 1,3 pentadiene
+ 2-butene + isobutylene

$\longrightarrow$ III' + 1 methyl-4-ethyl cyclohexene + propylene
+ m-xylene + ethylene

$\longrightarrow$ III' + 1,4 dimethyl cyclohexene + 1,3 butadiene
+ 2 methyl-1, 3-butadiene + acetylene
+ propylene

$\longrightarrow$ VI' + ethylene (11)

$\longrightarrow$ VI' + methyl cyclopentene

$\longrightarrow$ VI' + m-xylene + propane + propylene
+ acetylene + ethane + isobutylene

From the vinyl radical III

III $\xrightarrow{1,3}$ III' + isoprene + dipentene

$\longrightarrow$ III' + 1 methyl-4-ethyl cyclohexene + propylene
+ m-xylene

$\longrightarrow$ III' + 1,4 dimethyl cyclohexene + toluene
+ 2 methyl-1-butene

$\longrightarrow$ II' + ethylene + propylene + isoprene
+ m-xylene

$\longrightarrow$ II' + 2-butene + isobutylene (12)
+ p-methyl-isopropenyl benzene

$\longrightarrow$ VI' + p-methyl-isopropenyl benzene + isobutylene
+ ethylene + propylene

From the alkenyl radical IV

$$
\begin{aligned}
\mathrm{IV} &\xrightarrow{1,3(2,4)} \mathrm{IV'} + \text{isoprene} \\
&\xrightarrow{1,3(6,8)} \mathrm{IV'} + \text{dipentene} \\
&\xrightarrow{\qquad} \mathrm{IV'} + \text{m-xylene} + \text{ethane} \\
&\xrightarrow{\qquad} \mathrm{IV'} + \text{m-xylene} + \text{ethylene} + \text{2 methyl-1-butene} \\
&\qquad\qquad + \text{isoprene} \\
&\xrightarrow{\qquad} \mathrm{IV'} + \text{1,4 dimethyl cyclohexene} + \text{toluene} \\
&\qquad\qquad + \text{2 methyl-1-butene} \\
&\xrightarrow{\qquad} \mathrm{I'} + \text{ethylene} \\
&\xrightarrow{\qquad} \mathrm{I'} + \text{1,4 dimethyl cyclohexene} + \text{1,3 butadiene} \\
&\xrightarrow{\qquad} \mathrm{I'} + \text{acetylene} + \text{2 methyl-1-butene} + \text{propylene} \\
&\xrightarrow{\qquad} \mathrm{V'} + \text{isoprene} + \text{3 methyl-1, 3-pentadiene} \\
&\xrightarrow{\qquad} \mathrm{V'} + \text{2-butene} + \text{ethylene} + \text{m-xylene}
\end{aligned}
\tag{13}
$$

From the allylic radical V

$$
\begin{aligned}
\mathrm{V} &\xrightarrow{\qquad} \mathrm{V'} + \text{isoprene} \\
&\xrightarrow{\qquad} \mathrm{V'} + \text{dipentene} + \text{1,4 dimethyl vinyl cyclohexene} \\
&\xrightarrow{1,3} \mathrm{V'} + \text{3 methyl-1, 2-butadiene} \\
&\xrightarrow{\qquad} \mathrm{I'} + \text{methyl cyclopentene} \\
&\xrightarrow{\qquad} \mathrm{I'} + \text{toluene} + \text{propylene} + \text{isobutylene} \\
&\qquad\qquad + \text{ethylene} + \text{isoprene} + \text{m-xylene} \\
&\xrightarrow{\qquad} \mathrm{I'} + \text{2 methyl-2-butene} + \text{isobutylene} \\
&\qquad\qquad + \text{m-xylene} + \text{ethylene} \\
&\xrightarrow{\qquad} \mathrm{IV'} + \text{m-xylene} + \text{ethylene} + \text{isobutylene} \\
&\qquad\qquad + \text{2-methyl-2-butene}
\end{aligned}
\tag{14}
$$

Finally, from the allylic radical VI

$$
\begin{array}{llll}
\text{VI} & \longrightarrow & \text{VI}' & + \text{ isoprene} \\
 & \longrightarrow & \text{VI}' & + \text{ dipentene } + \text{ 1,5 dimethyl vinyl cyclohexene} \\
 & \xrightarrow{1,2} & \text{II}' & + \text{ dimethyl acetylene} \\
 & \longrightarrow & \text{II}' & + \text{ m-xylene } + \text{ ethylene } + \text{ 2-butene} \\
 & & & + \text{ methyl cyclopentene} \\
 & \longrightarrow & \text{III}' & + \text{ methyl cyclopentene} \\
 & \longrightarrow & \text{III}' & + \text{ toluene } + \text{ propylene } + \text{ ethylene} \\
 & & & + \text{ 2-butene } + \text{ 2 methyl-2-butene} \\
 & \longrightarrow & \text{III}' & + \text{ 1,4 dimethyl cyclohexene } + \text{ acetylene} \\
 & & & + \text{ 2-butene}
\end{array}
\tag{15}
$$

Chain Termination

Termination is thought to occur either by disproportionation or combination of the radicals in different combinatory paths. For example, the disproportionation between radicals I and II is illustrated in Equation 16.

$$
\begin{array}{l}
-CH_2-CH=\overset{\displaystyle CH_3}{\overset{|}{C}}\cdot \quad + \quad \cdot CH_2-CH_2-CH=\overset{\displaystyle CH_3}{\overset{|}{C}}-CH_2- \longrightarrow \\
-CH_2-CH=CH-CH_3 \quad + \quad CH_2=CH-CH=\overset{\displaystyle CH_3}{\overset{|}{C}}-CH_2-
\end{array}
\tag{16}
$$

Equation 17 shows the combination of allylic radicals V and VI.

$$
\begin{array}{l}
-CH_2-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_2\cdot \quad + \quad \cdot CH_2-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_2- \longrightarrow \\
-CH_2-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_2-CH_2-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_2-
\end{array}
\tag{17}
$$

The formations of m-xylene and toluene can be attributed to secondary reactions involving 1,3 dimethyl cyclohexadiene and methyl cyclohexene respectively. The two latter compounds are predicted in the above mechanisms but were not found experimentally.

A $C_{10}H_{12}$ hydrocarbon, p-methyl-isopropenyl benzene is predicted but was not found. It could be the secondary product of dipentene. Finally, the $C_{15}H_{24}$ hydrocarbons are possibly trimers of isoprene.

As seen from the above mechanisms, radicals I through VI all contributed to the formations of products in the pyrolysis of PI. However, only the allylic radicals V and VI contributed the most since they were the primary sources of isoprene and dipentene. It should be pointed out although isoprene and dipentene could also be formed from radicals III and IV, the hydrogen transfer processes involved had rendered these radicals less favorable than the allylic radicals V and VI for the formation of these two products.

The activation energy for the pyrolysis of PI in this work was found to be 41 Kcal $mole^{-1}$. This is low when compared to that reported by Madorsky[23] who obtained an activation energy of 56 Kcal $mole^{-1}$ for natural rubber in the temperature range from 290°-$306^{\circ}C$. The result can be explained by the presence of tertiary hydrogens from the 3,4 units in the sample used in this study. These tertiary hydrogens were especially susceptable to oxygen attack, thus decreasing the activation energy of chain initiation and increasing the overall activation energy.

Conclusion

Pyrolysis-GC-MS had been used to study PI. The major products were isoprene and dipentene which occupied almost 90 percent by weight of the total volatiles when completely pyrolyzed at 384°C (10 min). The ratio of dipentene to isoprene decreased with increase in pyrolysis temperatures.

A simple mechanistic scheme was proposed which involved α and β scissions of the polymer chain to account for all of the products. In general, products could be formed from radicals resulting from both types of scissions, however, those from β scissions, the allylic radicals were responsible for the formation of isoprene and dipentene. This led to the conclusion that the β bonds are weaker than the α bonds of the polymer chain.

Products reported by different investigators differ from one another because of variations in experimental conditions and samples employed. In this study, secondary reactions were minimized by conducting the pyrolysis in a sweeping atmosphere. However, m-xylene and toluene are believed to be secondary products.

Finally, the activation energy obtained in this work was lower than that reported in the literature. This was mainly due to the presence of 3,4 units in the polymer sample used.

Acknowledgement

The author would like to thank Dr. N. Calderon of the Goodyear Tire & Rubber Company for supplying the Natsyn 2200 polyisoprene sample.

References

1. Williams, C.G., Phil. Trans., 150, 241, 1860

2. Staudinger, H., Fritschi, J., Helv. Chim. Acta., 5, 785, 1922

3. Staudinger, H., Geiger, E., Helv. Chim. Acta., 9, 549, 1926

4. Midgley, T., Jr., Henne, A.L., J. Am. Chem. Soc., 51, 1215, 1929

5. Boonstra, B.B.S.T., Van Amerongen, G.J., Ind. Eng. Chem., 41, 161, 1949

6. Madorsky, S.L., Straus, S., Thompson, D., Williamson, L., J. Res.NBS, 42, 499, 1949

7. Straus, S., Madorsky, S.L., J. Res. NBS, 50, 165, 1953

8. Straus, S., Madorsky, S.L., Ind. Eng. Chem., 48, 1212, 1956

9. Jernejcic, M., Premu,L., Rubber Chem. Technol., 41, 411, 1968

10. Galin-Vacherot, M., European Polymer J., 7, 1455, 1970

11. Balogh, G.F., Goodyear Tire and Rubber Company, private communication

12. Dietz, W.A., J. of Gas Chromato., 68, 1967

13. Madorsky, S.L., Straus, S., Thompson, D., Williamson, L., J. Polymer Sci., 8, 639, 1949

14. Van DeWeil, H.J., Tommassen, P., J. of Chromato., 71, 9, 1972

15. Vacherot, M., Marchal, J., Rubber Chem. Technol., 41, 418, 1968

16. Hulot, H., Lebel, P., Rev. Gen. Caout., 40, 969, 1963

17. Banerjee, B.M. Singh, K., Nigam, R.K., Labdev J. Sci. Tech., 7A, 116, 1969

18. Binder, J.L., Ransaw, H.L., Anal. Chem., 29, 503, 1957

19. Hackathorn, M.J., Brock, M.J., J. Polymer Sci., Part B, 8, 617, 1970

20. Galin, M.J., Macromol. Sci.-Chem., A7, 873, 1973

21. Bolland, J.L., Orr, W.J.C., Trans. Inst. Rubber Ind., 21,133, 1945

22. Jellinek, H.H.G., 'Degradation of Vinyl Polymers', 173, Academic Press, 1955

23. Madorsky, S.L., 'Thermal Degradation of Organic Polymers', 225, Interscience, 1964

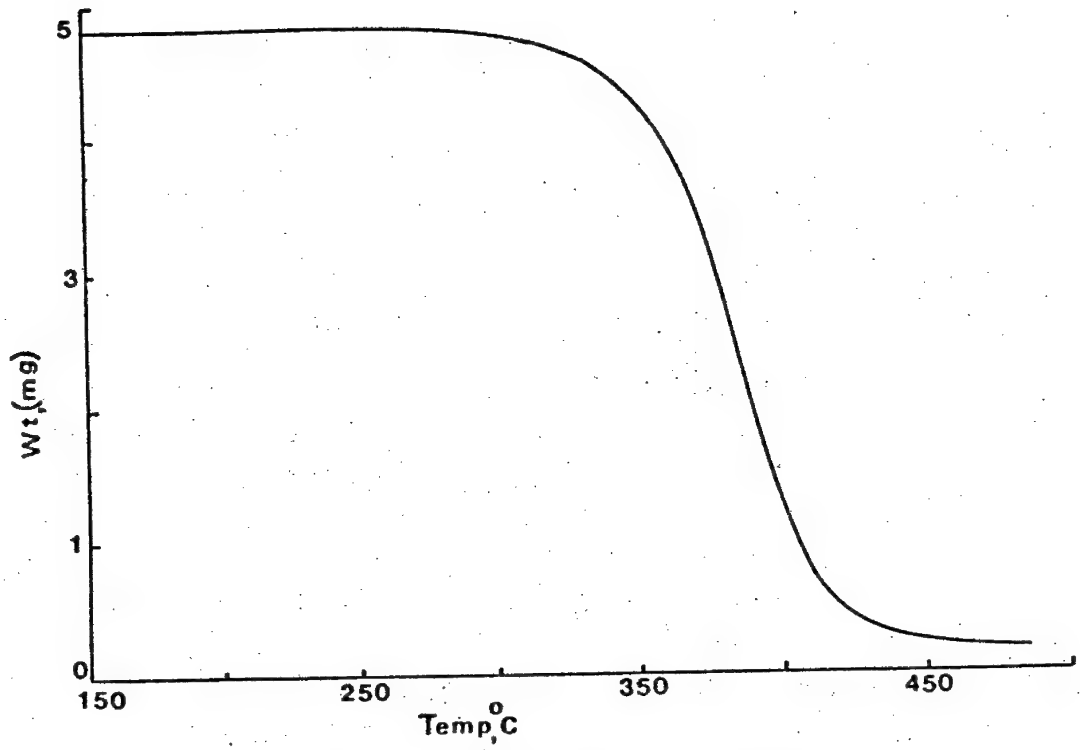


Fig. 1 TGA thermogram of PI in nitrogen

PLEASE NOTE:

In all cases this material has been filmed in the best possible way from the available copy. Problems encountered with this document have been identified here with a check mark ✓.

1. Glossy photographs ______
2. Colored illustrations ______
3. Photographs with dark background ______
4. Illustrations are poor copy ______
5. Print shows through as there is text on both sides of page ______
6. Indistinct, broken or small print on several pages ✓ throughout ______
7. Tightly bound copy with print lost in spine ______
8. Computer printout pages with indistinct print ______
9. Page(s) ______ lacking when material received, and not available from school or author ______
10. Page(s) ______ seem to be missing in numbering only as text follows ______
11. Poor carbon copy ______
12. Not original copy, several pages with blurred type ______
13. Appendix pages are poor copy ______
14. Original copy with light type ______
15. Curling and wrinkled pages ______
16. Other ______

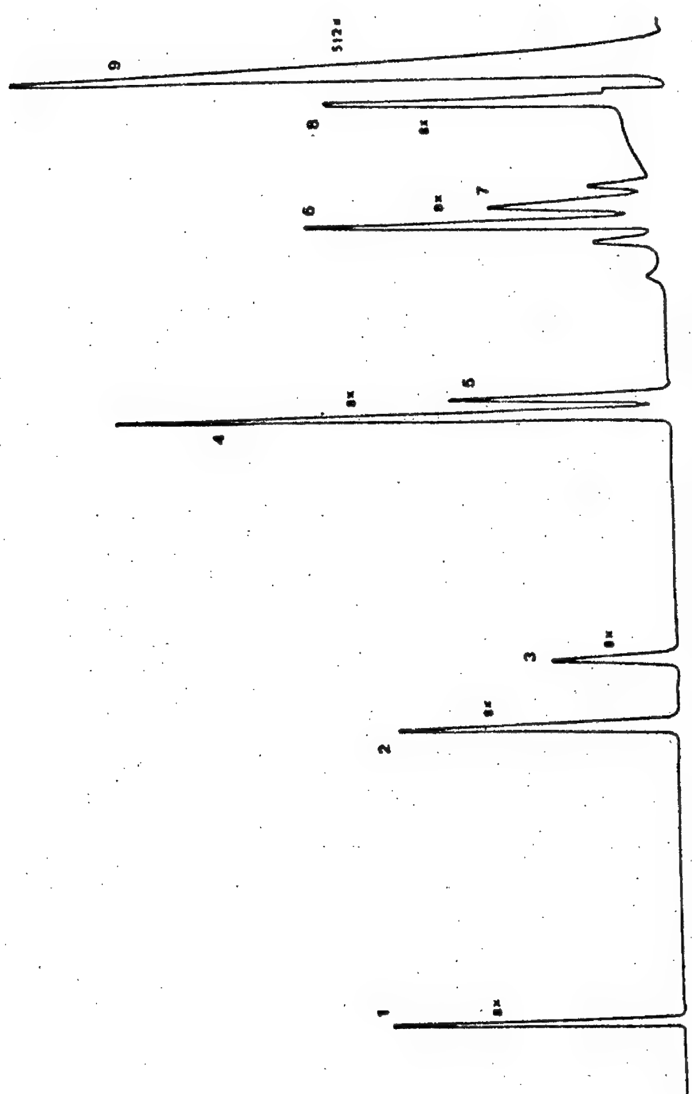


FIG.2 LOW-BOILING GC PYROGRAM OF PI IN HELIUM AT 384°C

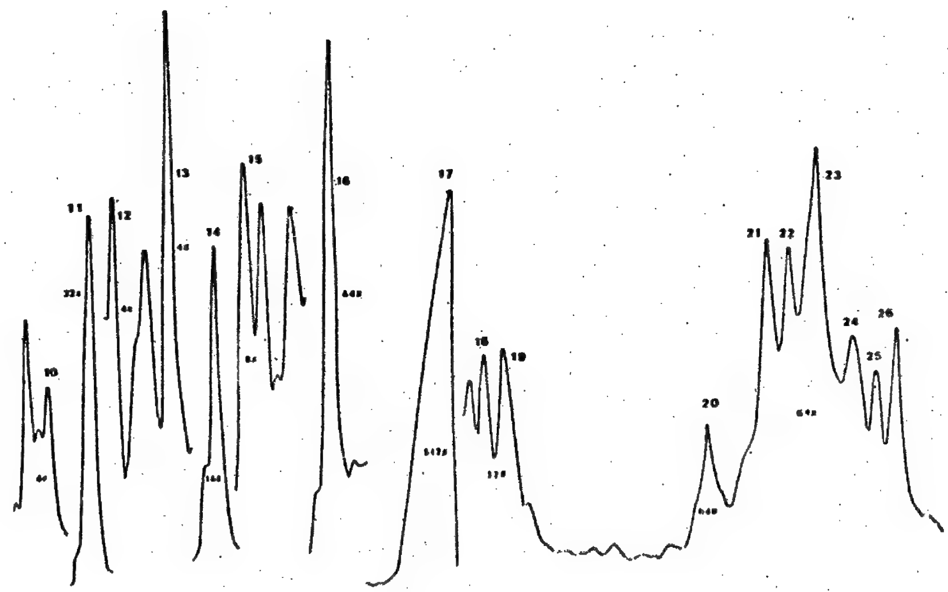


Fig. 3 High-boiling GC pyrogram of pyrolysis of PI in He at 384°C

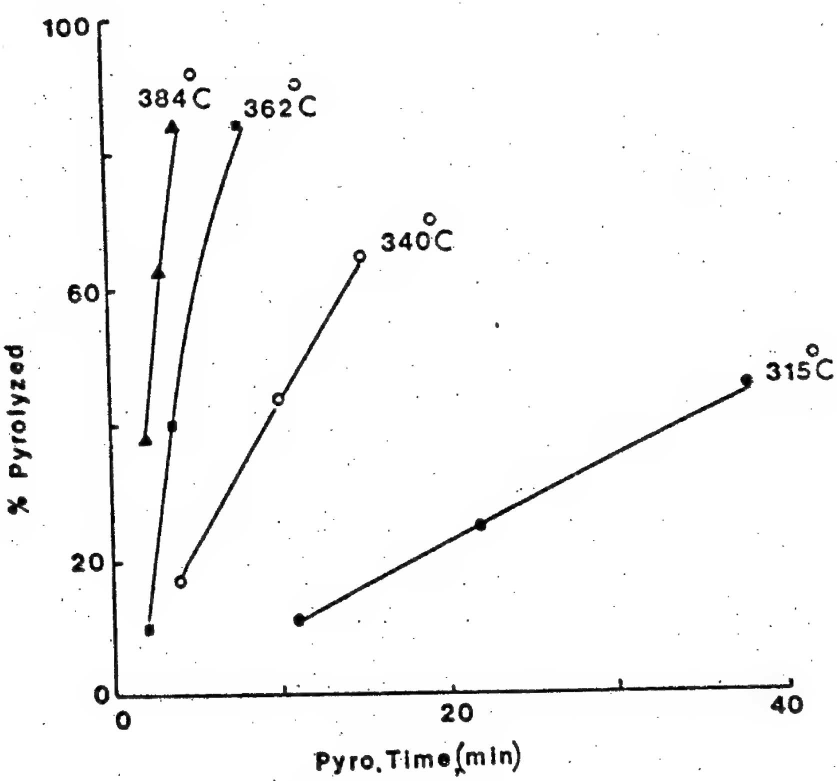


Fig. 4 Rates of pyrolysis of PI in helium
at indicated temperatures

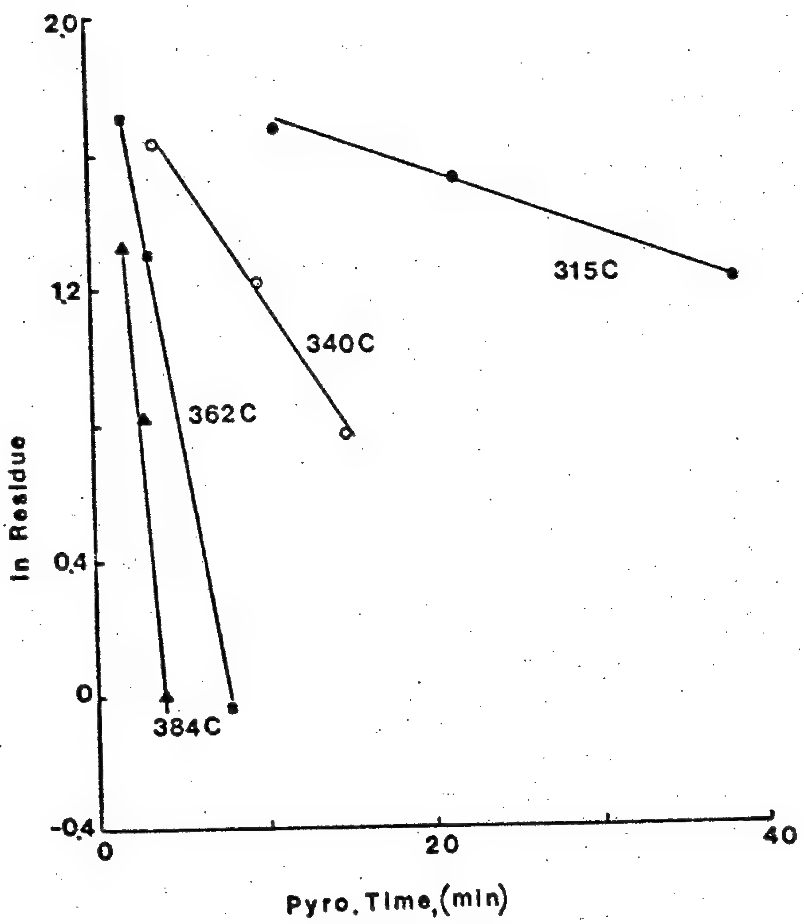


Fig. 5 First-order kinetic semilog plot of pyrolysis of PI in helium at indicated temperatures

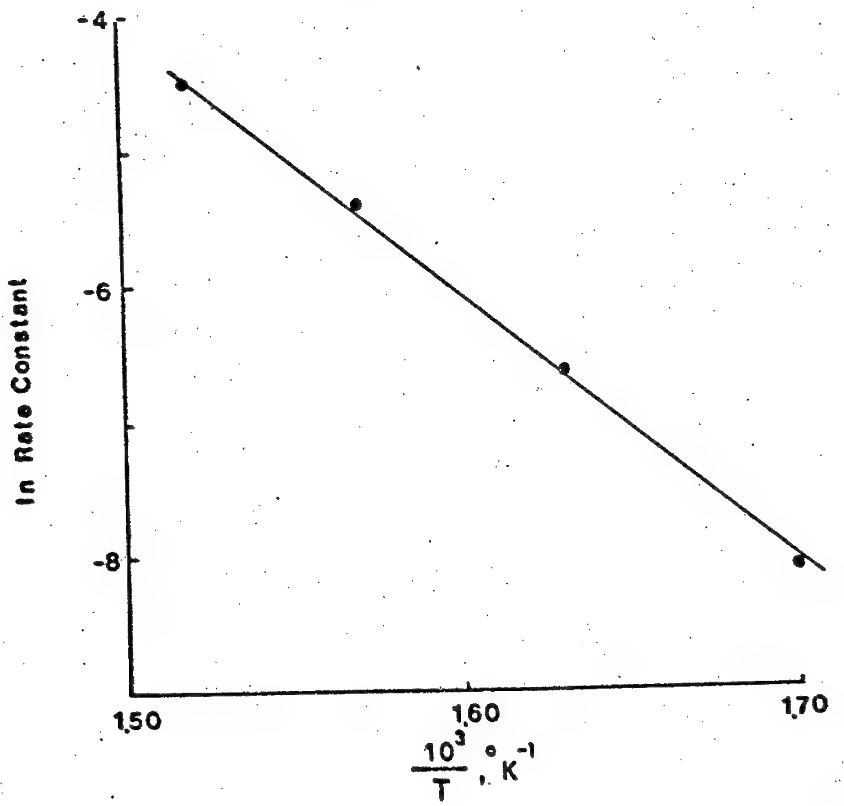


Fig. 6 Arrhenius plot for pyrolysis of PI in helium

CHAPTER VIII

OXIDATIVE PYROLYSIS OF POLYISOPRENE

Abstract

Natsyn 2200 polyisoprene(PI) was pyrolyzed in air from 260°-340°C with a novel interfaced gas chromatographic peak identification system (IPGCS). Pyrolytic products were separated by temperature programmed gas chromatography(GC) and analyzed by mass spectrometry(MS).

The ignition characteristics of PI were studied in air by thermogravimetric analysis(TGA) and by differential thermal analysis(DTA). The oxidative pyrolysis of polyisoprene followed first-order reaction kinetics. The rates of decomposition at different temperatures were determined and an activation energy of 27 Kcal mole^{-1} was obtained for the process.

The main pyrolytic products (up to C_4) were ketones, aldehydes, and hydrocarbons. The latter are believed to result from intramolecular chain transfer processes or from thermal decarboxylation of acids. Methanol was the only alcohol identified in significant amount. A simple mechanistic scheme was proposed which involved C-C scissions of the terminal and backbone alkoxy radicals accompanied by ·H and ·CH_3 transfers to account for all of the products.

Introduction

Much of the present knowledge of the oxidation of PI is based on the more precise studies that are possible with model compounds which are usually alkenes, cyclenes, and oligmers such as squalene.

Almost all commercial poly(diene)s have structural irregularities such as 1,2 or 3,4 linkages, cyclic structures, head-head and tail-tail linkages, and conjugated polyenes which can exist at the ends or along the length of the polymer chain. Although the concentration of these defects is usually very small, yet they can always affect the oxidation of the polymer. For example, the presence of 3,4 linkages in PI introduces tertiary hydrogens which are easily abstracted and are potential sites for oxygen attack.

Campbell[1] had shown that the infusion of a conjugated triene or a conjugated tetrene in peroxide-cured rubber increased the rate of thermal oxidation. According to this author, conjugated polyenes form a labile oxidation product, probably a polyperoxide, capable of oxidizing PI chain. Hence, polymer irregularities introduce uncertainties in using model compounds in the understanding of the chemistry of the oxidation of PI. As a result, different mechanisms have been reported.

A lot of studies have been reported in the aging and oxidation of PI at temperatures in the vicinity of 100°C, however, there is as yet no significant work done at high temperatures which is essential for applications requiring flame resistance. At high temperatures, thermal degradation coupled with severe oxygen attack on the polymer cause extensive cleavage of C-C and C-H bonds resulting in fragments which are potentially flammable.

In this work, pyrolysis-GC-MS was used to study the oxidative pyrolysis of PI. The IPGCS employed was described in Chapter III. The mechanisms of the pyrolysis process were discussed according to the nature of the products. The ignition characteristics of the polymer in air were investigated by TGA and DTA. The kinetics of the oxidative pyrolysis of this polymer were also examined.

Experimental

Natsyn 2200 (Goodyear) PI, employed in the pyrolysis experiment in the previous Chapter, was also used in the present work.

The pyrolysis temperatures were determined by TGA (DuPont 900 thermal analyzer) in air at a flow rate of 25 ml min^{-1} and a heating rate of 30°C min^{-1}. To investigate its ignition characteristics, the experiment was repeated at an air flow rate of 60 ml min^{-1} at the same heating rate. The result was compared to that of DTA (plug-in module for DuPont 900 thermal analyzer) under similar conditions.

About 6 mg of sample was used in each pyrolysis experiment. The polymer was pyrolyzed with MP3 in air at a flow rate of 25 ml min^{-1} at 268°, 290°, 315°, and 340°C respectively. The procedures were similar to those as described in the previous Chapter. A Chromosorb 102 column (12 ft x 1/8" O.D.) was used to separate the products with flame ionization detection. The products were identified by MS. The oxidative pyrolysis of PI followed first-order reaction kinetics. The rates of decomposition and the corresponding activation energy for the process were determined.

Results

Figure 1 compares the TGA curves of PI in air at flow rates of 25 ml min^{-1} and 60 ml min^{-1} at a heating rate of 30°C min^{-1}. Figure 2 shows the DTA of PI in air at a flow rate of 60 ml min^{-1} at the same heating rate. Figure 3 shows the pyrogram obtained with the Chromosorb 102 column at 388°C. The numbers followed by x signs represent the detector attenuation factors and those adjacent to each peak refer to the peak numbers in Table 1. This Table shows the MS fragmentation patterns of those products that were found in significant amounts experimentally. The underlined mass numbers represent the most abundant species.

Figures 4 and 5 show the results of the rate of oxidative pyrolysis of PI and the first-order kinetic semilog plot. The corresponding Arrhenius plot is shown in Figure 6. Table 2 summarizes the results of the kinetic studies of the oxidative pyrolysis of PI.

Discussion of Results

The aging and oxidative degradation of PI have been the subject of numerous studies. The investigations of the autoxidative degradation of natural rubber dated back more than a century[2]. The formation of peroxide groups in this process was demonstrated as early as 1915[3].

Various mechanisms have been proposed for the chain scission reactions of rubbers. Bolland et al.[4,5] proposed that an unstable β-peroxyalkoxy radical was formed and decomposed by a sequence of steps to account for the products. Bevilacqua[6-8] formulated a mechanism for scission basing on the products of oxidation and oxygen consumption in the oxidation

Table 1

Fragmentation Patterns of Products from Oxidative Pyrolysis of PI at 388°C

Peak number	Product	Fragmentation pattern
-	Carbon dioxide[a]	44, 28
1	Ethylene	28, 27, 26
2	Ethane	30, 29, 28, 27, 26
-	Water[a]	18, 17, 16
3	Propylene	42, 41, 39, 27
4	Propane	44, 43, 29, 28, 27
5	Formaldehyde	30, 29, 28
6	Methanol	32, 31, 29, 15
7	Acetaldehyde	44, 43, 42, 29
8	Acrolein	56, 41, 39, 27
9	Propan-1-al	58, 43, 41, 29
10	Acetone	58, 43, 28
11	Methacrolein	70, 55, 41, 39, 29
12	Methyl Vinyl Ketone	70, 68, 67, 53, 42, 41, 40, 29, 27
13	Butan-1-al	72, 50, 42, 41, 39, 29
14	Methyl ethyl Ketone	72, 55, 43, 42, 39, 27

[a]Detected by MS

Table 2

Kinetic Results of the Oxidative Pyrolysis of PI

Temp, °C	Rate Constants, sec $^{-1}$
268	4.0×10^{-4}
290	6.3×10^{-4}
315	4.0×10^{-3}
340	5.8×10^{-3}
Activation Energy, Kcal mole^{-1}	27

of latex and of dry rubber. This author concluded that the efficiency of chain scission of natural rubber by molecular oxygen increased rapidly with increase in temperature to a limiting value of about 6.2 molecules of oxygen per bond cleaved. This value is close to the theoretical for destruction of one isoprene unit per chain cut. In a separate work, Bevilacqua et al.[9] studied the oxidation of cis PI at 120°C and products boiling lower than water were identified by comparison with GC retention times and infrared spectra of authentic compounds.

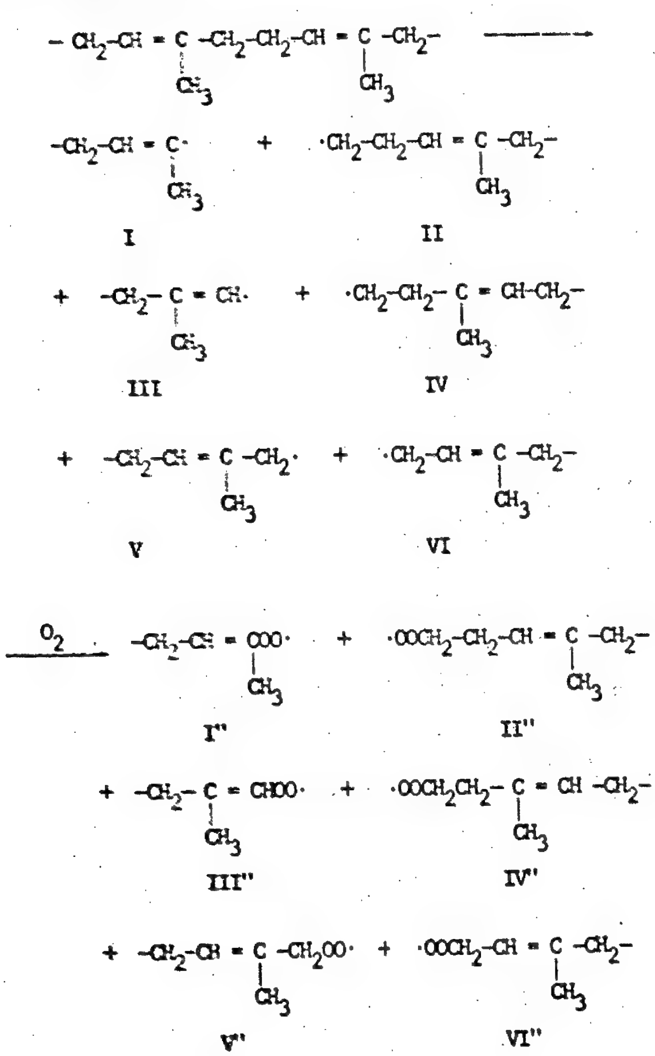
Amerongen[10] compared the oxidative and non-oxidative thermal degradation of rubber and concluded that at moderately high temperature, the deterioration of rubber was due not only to oxidation but thermal decomposition as well. Scheele et al.[11] studied the oxidation of cis 1,4 PI at 120°-150°C and found methyl vinyl ketone, methyl ethyl ketone, methacrolein, and acetone as major products. Minor products included methanol, acetic acid, and acetylene. These authors concluded that stereochemistry had no influence on oxidation mechanisms since natural rubber, cis and trans PI all gave the same products.

Voigt and Krueger[12] at moderately low temperatures found acetylene, acetone, methanol, and vinyl acetylene as the oxidative degradation products of PI. These authors suggested two possible mechanisms for the oxidative chain cleavage of the polymer, one in which the primary oxygen attack occurred at both allylically activated α-methylene groups, and a second in which attack occurred preferentially on the α-methylene group next to the methyl-substituted carbon.

Morand[13] reported the oxidative degradation of PI at 100°C (3 hours) and obtained 26 products by GC. Product identifications were obtained by comparing GC retention times, infrared, nuclear magnetic resonance and mass spectra with those of authentic compounds. More recently, the effect of molecular weight on the rate of oxidative degradation of natural rubber at 125°C was examined by Safronova et al.[14]. These authors concluded that the rate increased gradually with the molecular weight of the sample and leveled out at a molecular weight of about 2×10^6.

The discussion of the above studies is not at all irrelevant here since most of the products identified in this work compare favorably with those obtained by Scheele, Voigt and Bevilacqua at temperatures from 120°-150°C. Despite the difference in temperature, fundamental reactions such as the formation and decomposition of hydroperoxides, C-C scissions, etc., are still the same. The complexity of the nature of the products from oxidative dagradation of PI had been shown by Morand[13]. In order to simplify the situation in this discussion, no attempt was made to identify products higher than C_4. A discussion of the mechanisms for their formation follows.

Chain Initiation



(1)

<u>Chain Propagation</u>

Radicals I''– VI'' can extract a hydrogen atom intermolecularly to give the corresponding hydroperoxides of transient stability. Loss of $\cdot OH$ leads to the respective alkoxy radicals I''' – VI'''. Scission of C-C bonds accompanied by $\cdot H$ or $\cdot CH_3$ transfer yields the products below where the numbers above the arrows indicate the particular C-C bond severed. The underlined products correspond to those found in significant amounts experimentally.

From I'''

$-CH_2-CH=C(CH_3)-CH_2-CH_2-CH=C(CH_3)-O\cdot \xrightarrow{1,3}$ IV + <u>Acrolein</u>

$\xrightarrow{3,4}$ V + $CH_2=C=C(OH)-CH_3$

+ <u>Methyl vinyl ketone</u> + <u>Methacrolein</u>

+ $CH_2=CH-C(OH)=CH_2$

+ $CH_3-CH=CH-CHO$ (2)

$\xrightarrow{4,5}$ I + Acetylene + <u>Acetone</u>

+ $CH_2=CH-CH=C(OH)-CH_3$

+ $CH_3-\dot{C}H=C=C(OH)-CH_3$

+ $CH_3-CH=CH-C(=O)-CH_3$

+ $CH_3-CH=CH-C(OH)=CH_2$

+ 3 methyl-4, 5-dihydrofuran

$\xrightarrow{5,7}$ IV + Methyl vinyl acetylene + <u>Acetone</u>

$+\ CH_3-CH=CH-CH_2-CH=CH-\underset{\underset{O}{\|}}{C}-CH_3$

$+\ CH_2=\underset{\underset{CH_3}{|}}{C}-CH_2-CH=CH-\underset{\underset{O}{\|}}{C}-CH_3$

$+\ CH_3-CH_2-CH=CH-\underset{\underset{O}{\|}}{C}-CH=CH-CH_3$

$+\ CH_3-CH_2-CH=CH-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{C}=CH_2$

$+\ CH_3-CH=CH-CH=CH-CH=\underset{\underset{OH}{|}}{C}-CH_3$ (2)

$+\ CH_2=\underset{\underset{CH_3}{|}}{C}-CH=CH-CH=\underset{\underset{OH}{|}}{C}-CH_3$

$+\ CH_3-CH=CH-CH=\underset{\underset{OH}{|}}{C}-\underset{\underset{CH_3}{|}}{C}=CH_2$

$+\ CH_3-CH=CH-\underset{\underset{OH}{|}}{CH}-CH=CH-CH_3$

From II''

$-CH_2-CH_2-\underset{\underset{CH_3}{|}}{C}=CH-CH_2-CH_2-O\cdot$

$\xrightarrow{1,2}$ V + <u>Formaldehyde</u>

$\xrightarrow{2,3}$ III + <u>Acetaldehyde</u> + $CH_2=CH-OH$ (3)

$\xrightarrow{3,5}$ II + Acetylene + <u>Acetone</u>

+ $CH_3-CH=CH-CH_2-CHO$

+ $CH_3-C\equiv C-CH_2CH_2OH$

+ $CH_2=\underset{\underset{CH_3}{|}}{C}-CH_2-CHO$

+ $CH_3CH=CH-CH_2-CHO$

+ $CH_3-CH=C=CH-CH_2-OH$

+ 2 methyl-5-hydrofuran

$\xrightarrow{5,6}$ VI + Methyl acetylene + Acetone (3)

+ $CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_2-CHO$

+ $CH_2=\underset{\underset{CH_3}{|}}{C}-CH=CH-CH_2-OH$

+ $CH_3-CH_2-CH=CH-CH_2-CHO$

+ $CH_3-CH=C=CH-CH_2-CH_2-OH$

+ 3 methyl-2,5,6-trihydropyran

From III'''

$$-CH_2-\underset{\underset{CH_3}{|}}{C}=CH-CH_2-CH_2-\underset{\underset{CH_3}{|}}{C}=CH-O\cdot$$

$\xrightarrow{1,3}$ II + Acrolein (4)

$\xrightarrow{3,4}$ VI + Methacrolein + Methyl vinyl ketone

+ $CH_3-CH=C=CH-OH$

+ $CH_2=CH-CH=CH-OH$

$\xrightarrow{4,5}$ III + Acetylene + <u>Acetone</u>

$+ \ CH_3CH = \underset{\displaystyle CH_3}{\underset{|}{C}} - CHO$

$+ \ CH_2 = CH - \underset{\displaystyle CH_3}{\underset{|}{C}} = CH - OH$

$+ \ CH_3 - CH_2 - CH = CH - CHO$

$+ \ CH_3 - CH_2 - CH = C = CH - OH$

+ 3 methyl-4,5 dihydrofuran

$\xrightarrow{5,7}$ II + Methyl vinyl acetylene + <u>Acetone</u>

$+ \ CH_3 - CH = CH - CH_2 - CH = \underset{\displaystyle CH_3}{\underset{|}{C}} - CHO$ (4)

$+ \ CH_2 = C = CH - CH_2 - CH_2 - \underset{\displaystyle CH_3}{\underset{|}{C}} = CH - OH$

$+ \ CH_2 = \underset{\displaystyle CH_3}{\underset{|}{C}} - CH_2 - CH = \underset{\displaystyle CH_3}{\underset{|}{C}} - CHO$

$+ \ CH_2 = \underset{\displaystyle CH_3}{\underset{|}{C}} - CH = CH - \underset{\displaystyle CH_3}{\underset{|}{C}} = CH - OH$

$+ \ CH_3 - \underset{\displaystyle CH_3}{\underset{|}{C}} = CH - CH_2 - CH = C = CH - OH$

$+ \ CH_3 - \underset{\displaystyle CH_3}{\underset{|}{C}} = CH - CH = CH - CH_2 - CHO$

$$+\ CH_3-CH=\underset{\underset{CH_3}{|}}{C}-CH_2-CH=C=CH-OH$$

$$+\ CH_3-CH=\underset{\underset{CH_3}{|}}{C}-CH=CH-CH_2-CHO \qquad (4)$$

+ 2,6 dimethyl-4, 5-dihydrooxepin

From IV'''

$$-CH_2-CH=\underset{\underset{CH_3}{|}}{C}-CH_2-CH_2O\cdot$$

$\xrightarrow{1,2}$ V + <u>Formaldehyde</u>

$\xrightarrow{2,3}$ I + <u>Acetaldehyde</u> + $CH_2=CH-OH$

$\xrightarrow{3,5}$ IV + Acetylene + <u>Acetone</u>

$$+\ CH_3-CH=CH-CH_2-CHO$$

$$+\ CH_2=C=CH-CH_2-CH_2-OH \qquad (5)$$

$$+\ CH_2=\underset{\underset{CH_3}{|}}{C}-CH_2-CHO$$

$$+\ CH_2=\underset{\underset{CH_3}{|}}{C}-CH=CH-OH$$

+ 2 methyl-4,5-dihydrofuran

From V'''

$$-CH=\underset{\underset{CH_3}{|}}{C}-CH_2-CH_2-CH=\underset{\underset{CH_3}{|}}{C}-CH_2-O\cdot$$

$\xrightarrow{1,2}$ I + <u>Formaldehyde</u>

$\xrightarrow{2,4}$ IV + Methacrolein + Methyl vinyl ketone

+ $CH_3-CH=CH-CHO$

$\xrightarrow{4,5}$ V + Acetylene + Acetone

+ $CH_3-CH=\underset{\underset{CH_3}{|}}{C}-CHO$ + $CH_2=CH-\underset{\underset{CH_3}{|}}{CH}-CHO$

+ $CH_3-CH_2-CH=CH-CHO$

+ $CH_2=CH-\underset{\underset{CH_3}{|}}{C}=CH-OH$

+ $CH_3-CH_2-CH=C=CH-OH$

+ 3 methyl-2,5-dihydrofuran (6)

$\xrightarrow{5,6}$ I + Methyl vinyl acetylene + Acetone

+ $CH_3CH_2CH=\underset{\underset{CH_3}{|}}{C}-CHO$

+ $CH_2=CH-CH=\underset{\underset{CH_3}{|}}{C}-CH_2-OH$

+ $CH_3-CH_2-CH_2-CH=CH-CHO$

+ $CH_3-CH=CH-CH=CH-CH_2-OH$

+ 3 methyl-2,5,6-trihydropyran

From VI'''

$$-\underset{\displaystyle CH_3}{\underset{|}{C}} = CH - CH_2 - CH_2 - \underset{\displaystyle CH_3}{\underset{|}{C}} = CH - CH_2O\cdot$$

$\xrightarrow{1,2}$ III + <u>Formaldehyde</u>

$\xrightarrow{2,4}$ II + <u>Methacrolein</u> + $CH_3-CH = CH-CHO$

+ <u>Methyl vinyl ketone</u>

$\xrightarrow{4,5}$ VI + Acetylene + <u>Acetone</u>

+ $CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}} = CH-CHO$ + $CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_2-CHO$

+ $CH_3-CH_2-CH = CH-CHO$

+ $CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH = CH-OH$

+ $CH_3-CH = C = CH-CH_2-OH$

+ 3 methyl-2,5-dihydrofuran (7)

$\xrightarrow{5,6}$ III + Methyl acetylene + <u>Acetone</u>

+ $CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}} = CH-CHO$

+ $CH_3-CH_2-CH_2-CH = CH-CHO$

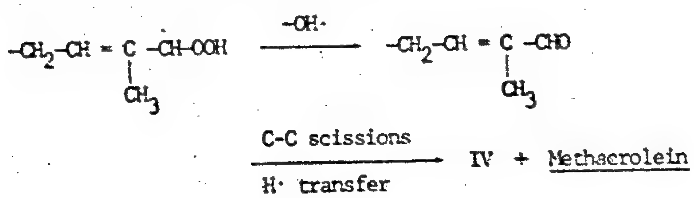
+ $CH_2 = CH-\underset{\displaystyle CH_3}{\underset{|}{C}} = CH-CH_2-OH$

+ $CH_3-CH_2-CH = C = CH-CH_2-OH$

+ $CH_3-CH = CH-CH = CH-CH_2-OH$

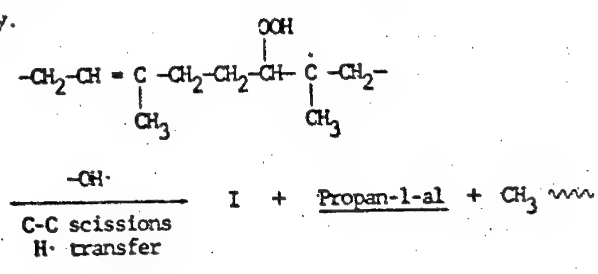
+ 4 methyl-2,5,6-trihydropyran

As in the oxidative pyrolysis of polypropylene discussed in Chapter V, intramolecular hydrogen abstraction, followed by loss of OH·, C-C scission, H· or ·CH_3 transfer and H· abstraction can lead to the same products as shown in the above reactions. This is illustrated for abstraction of an allylic hydrogen by radical V'.

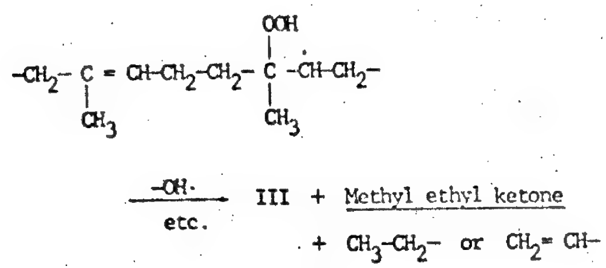


(8)

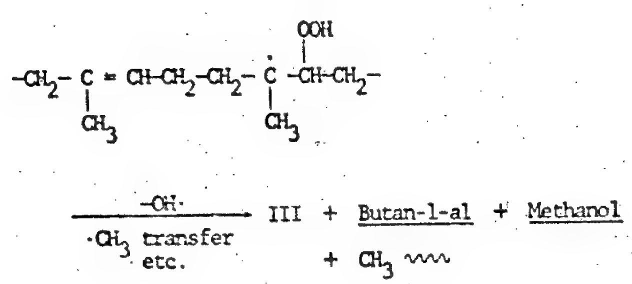
It should also be pointed out that while the terminal radicals are responsible for product formations, similar reactions may occur through backbone radicals as well. These radicals can be formed by direct oxygen attack at either the unsaturated center or at the alpha methylene. This is illustrated for the formations of methanol, propan-1-al, butan-1-al, and methyl ethyl ketone which were found in significant amounts in this study.



(9)



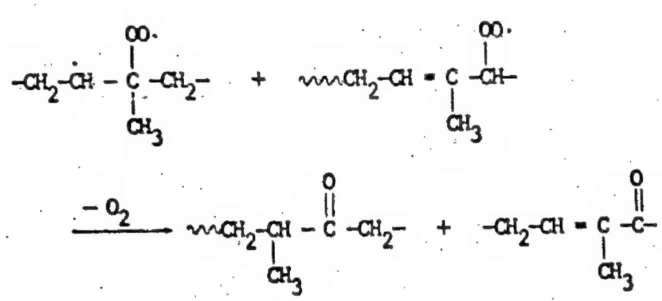
(10)



(11)

Chain Termination

This can occur either by disproportionation or by combination of the radicals resulting from the above chain propagation steps in a similar manner as described in Chapter VII (Equation 16, 17). Termination may also occur by a bimolecular process such as shown in Equation 12.



(12)

Scheele[11] and Voigt[12] found acetylene and vinyl acetylene, these products were predicted but not found experimentally. Buten-2-al, found by Morand[13] was also predicted but owing to its relatively high boiling point(105°C), it was not separated by the Chromosorb 102 column under the experimental conditions prescribed. Almost all of the other C_3 and C_4 aldehydes and ketones were identified. Methanol was the only alcohol found in significant amount. No acids were identified in significant quantities, it is believed that they decarboxylated into hydrocarbons and CO_2 at the temperatures employed in this study.

The TGA of PI in air at 25 ml min^{-1} showed no sudden weight loss which is usually associated with the ignition of the sample. However, at 60 ml min^{-1}, the sample ignited at about 370°C as evidenced by a rapid weight loss at this temperature. The ignition was confirmed by the strong exothermic peak at about the same temperature in DTA. The ignition at high air flow could be either due to an increase of oxygen supply or to the turbulence created by the flow. The latter situation best simulates the ignition of polymeric materials in actual fire.

The activation energy for the oxidative pyrolysis of PI in this work was 27 Kcal $mole^{-1}$. Shelton[15] had shown that the activation energy for the oxidative degradation of Hevea rubber between 50°-100°C was in the range of 24-26 Kcal $mole^{-1}$ and the same mechanism was found to extend over the entire temperature range. Considering the similarity of low-boiling products between this work and other reported studies[11,12,13] at moderately low temperatures, there is reason to believe that the basic degradation mechanism should not be too different despite the huge difference in temperatures. However, an increase in temperature certainly increases the rate of the degradative process.

Conclusion

Oxidative pyrolysis-GC-MS was used to study PI at temperatures from 268°-340°C. The major products were aldehydes and ketones. Methanol was the only alcohol represented under the prescribed experimental conditions. Some hydrocarbons were identified and they are believed to be formed either by the intramolecular chain transfer processes or by the thermal decarboxylation of acids.

The oxidative pyrolysis of PI followed first-order reaction kinetics and an activation energy of 27 Kcal $mole^{-1}$ was obtained. The similarity of the products between this work and other reported studies at moderately low temperatures suggests that the same basic mechanism may occur at both low and high temperatures. Finally, a mechanistic scheme was proposed to account for all of the products. This scheme involved C-C scissions of the terminal and backbone alkoxy radicals accompanied by H· and $\cdot CH_3$ transfers.

References

1. Campbell, D.S., J. Appl. Poly. Sci., 13, 1013, 1969
2. Hofmann, A.W., J. Chem. Soc., 13, 87, 1861
3. Davis, C.C., Blake, J.T., ed., 'Chemistry and Technology of Rubber', Reinhold, N.Y., 1937
4. Bolland, J.L., Hughes, H., J. Chem. Soc., 499, 1949
5. Bolland, J.L. Ten Have, P., Trans. Faraday Soc., 45, 93, 1949
6. Bevilacqua, E.M., J. Am. Chem. Soc., 77, 5396, 1955; 79, 2915, 1957; 80, 5346, 1958
7. Bevilacqua, E.M., J. Org. Chem., 21, 369, 1956
8. Bevilacqua, E.M., Rubber Age, 80, 271, 1956
9. Bevilacqua, E.M., English, E.M., Gall, E.S., Norling, P.M., J. of Appl. Poly. Sci., 8, 1029, 1964
10. Amerongen, G.J. van, Rubber Chem. Technol., 29, 857, 1956
11. Scheele, W., Voigt, H.U., Kaut. Gummi. Dunstst., 22, 467, 1969
12. Voigt, H.U., Krueger, F.U., Kaut. Gummi. Kunstst., 24, 399, 1971; 25, 133, 1972
13. Morand, J.L., Rubber Chem. Technol., 47, 1094, 1974
14. Safronova, G.S., Betts, G.E., Zhakove, V.G., Karmin, B.K., Kauch. Rezina, 18, 1977
15. Shelton, J.R., Rubber Chem. Technol., 30, 1268, 1957

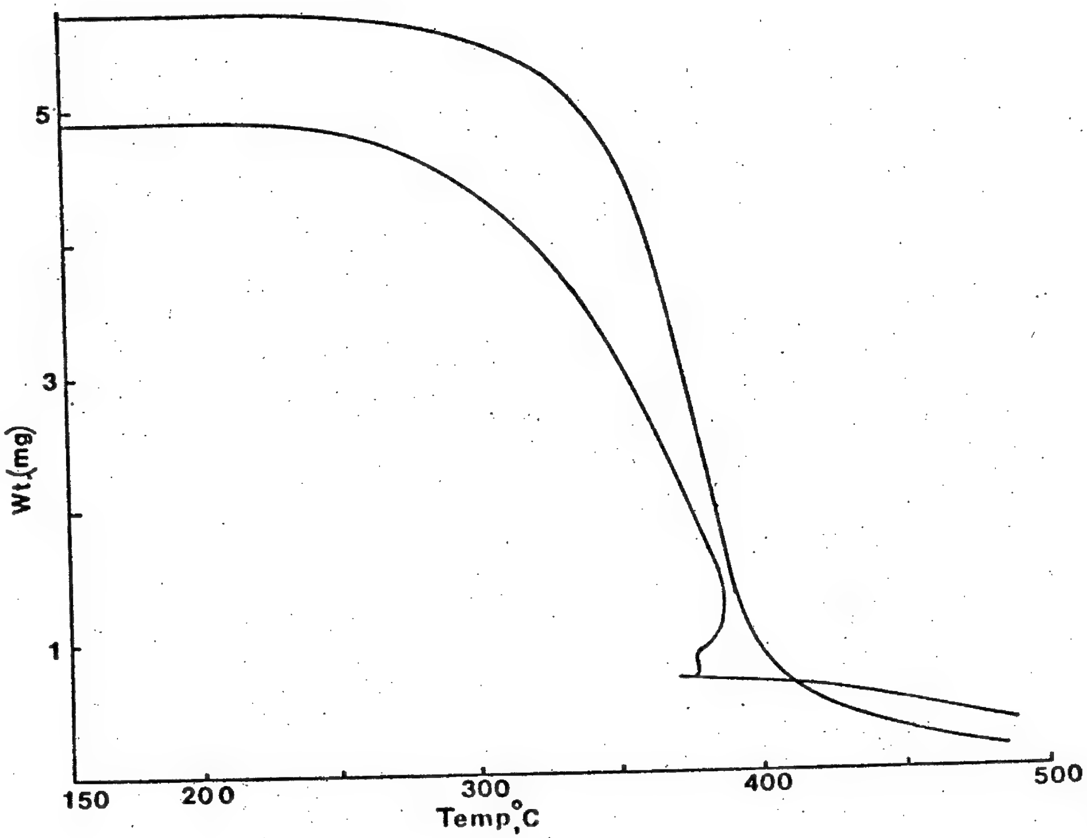


Fig. 1 TGA thermograms of PI in air

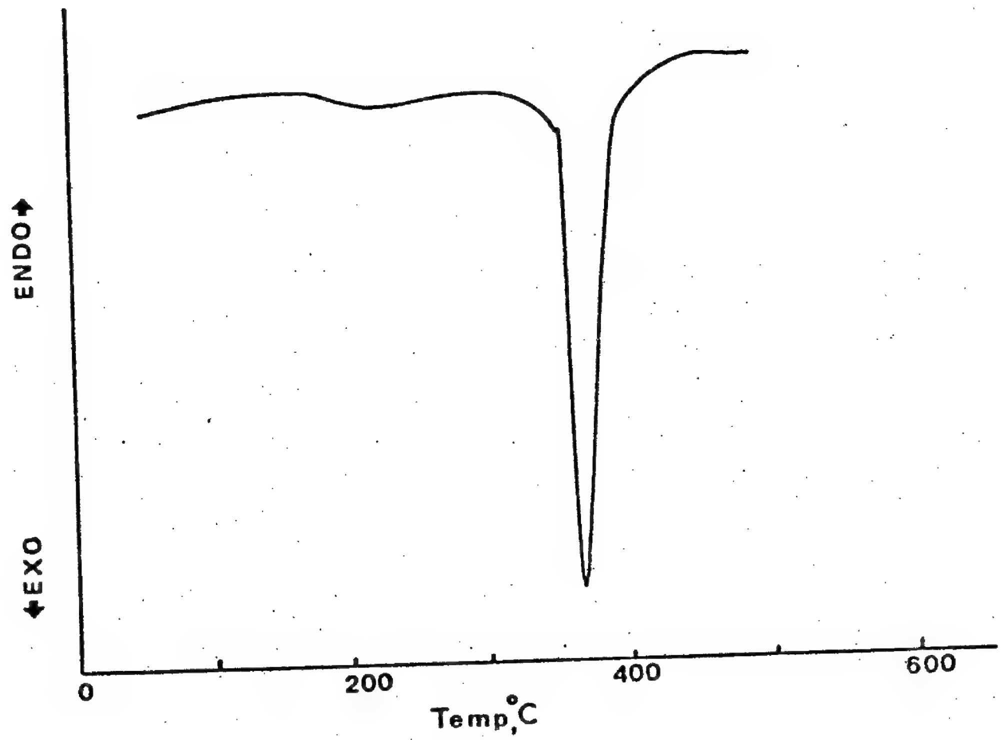


Fig. 2 DTA thermogram of PI in air

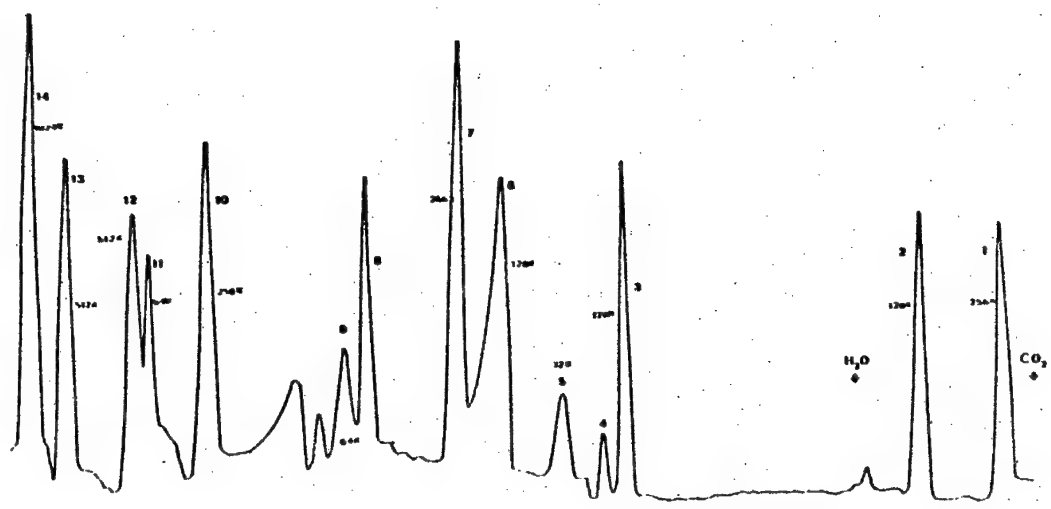


Fig. 3 Low-boiling GC pyrogram of pyrolysis of PI in air at 338°C

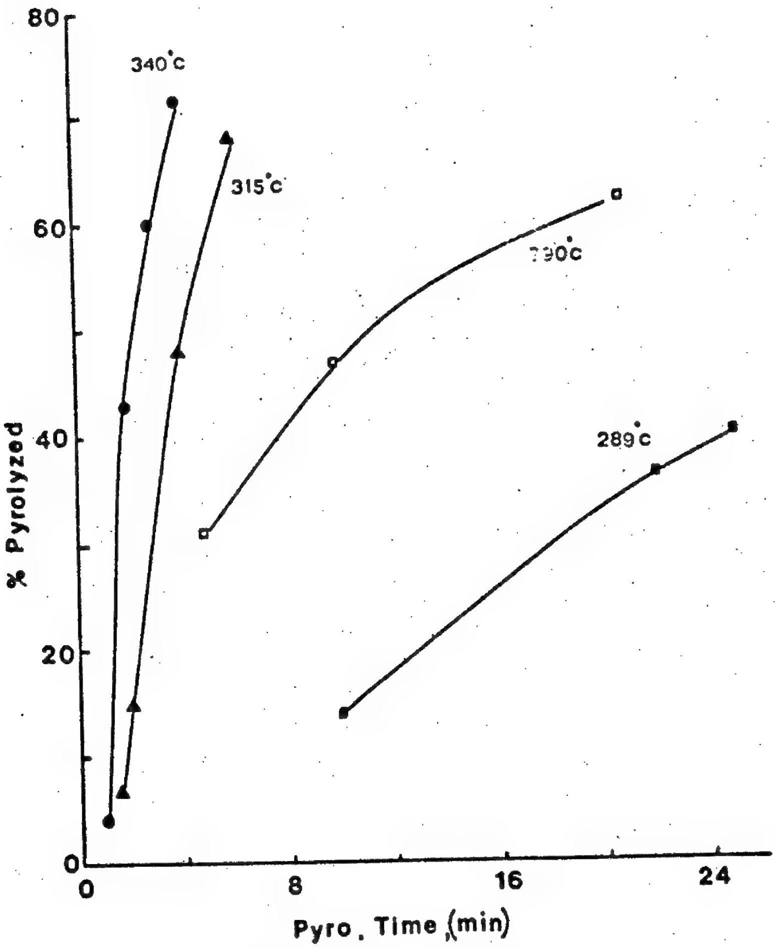


Fig. 4 Rates of pyrolysis of PI in air at indicated temperatures

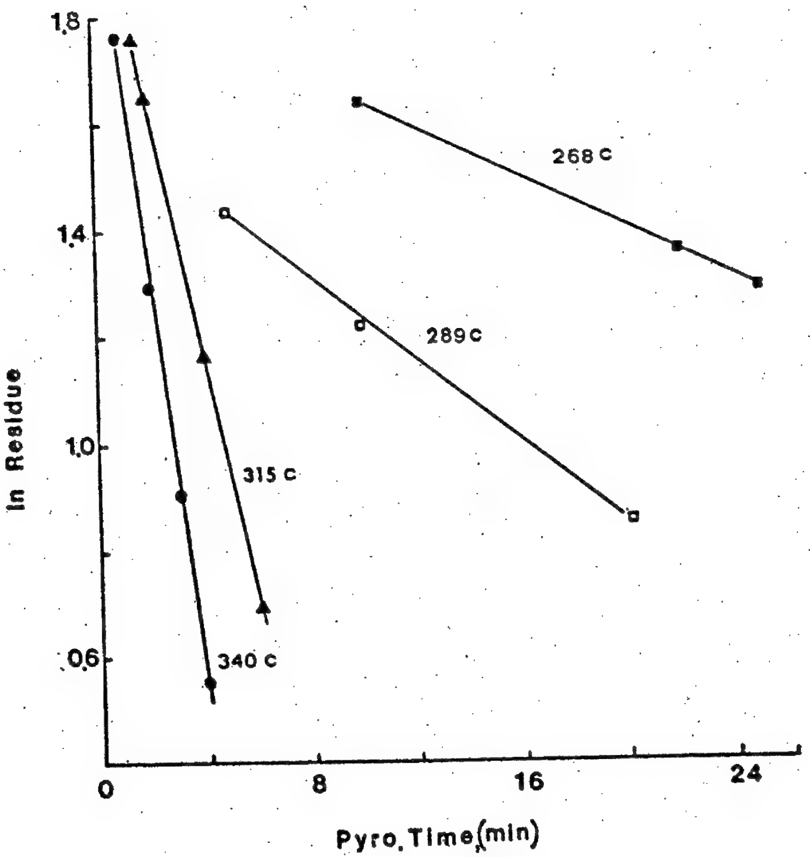


Fig. 5 First-order kinetic semilog plot for pyrolysis of PI in air at indicated temperatures

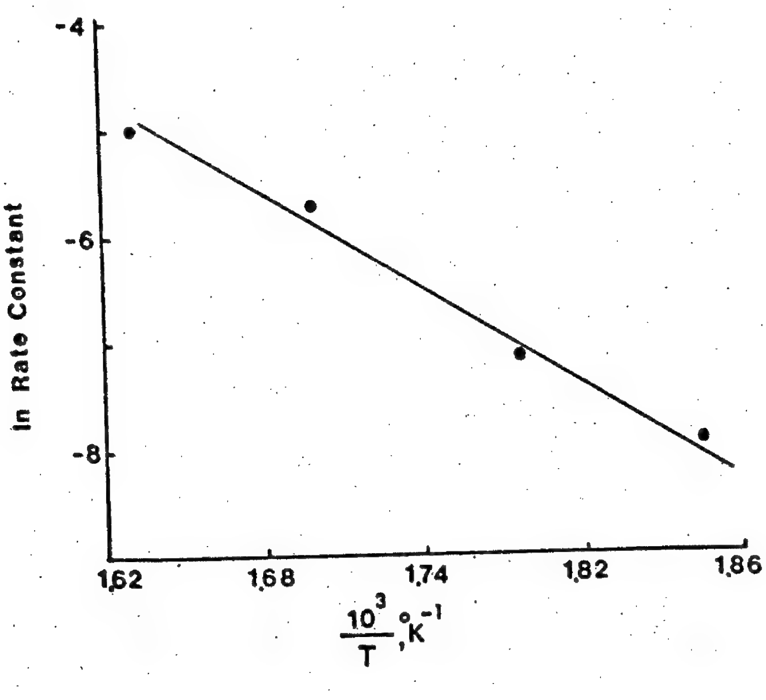


Fig. 6 Arrhenius plot for pyrolysis of PI in air

CHAPTER IX

EFFECT OF VANADIUM ON PYROLYSIS AND OXIDATIVE PYROLYSIS OF POLYISOPRENE

Abstract

Natsyn 2200 polyisoprene(PI) was hydroxylated with peracetic acid and reacted with vanadium oxytrichloride($VOCl_3$) to form a vanadium-coordinated polyisoprene(VPI).

The thermal stabilities and ignition characterisitcs of VPI in inert and in oxidative atmospheres were studied by thermogravimetric analysis(TGA) and differential thermal analysis(DTA). Pyrolysis and oxidative pyrolysis of VPI were conducted with a novel interfaced pyrolysis gas chromatographic peak identification system. The processes followed first-order reaction kinetics. The rates of decomposition and the corresponding activation energies were compared to those obtained for neat PI. The presence of vanadium in the polymer was found not to affect the nature of the products.

The thermal stability of VPI and PI was very similar in inert atmosphere in the temperature range studied. Both polymers acquired an activation energy of about 40 Kcal mole^{-1}. Product distributions, however, were very different between the two polymers. VPI was found to form less volatiles (peak areas up to C_{16}) than PI.

In oxidative environment, VPI was more stable than neat PI resulting in lower rates of decomposition and a higher activation energy (50 Kcal mole^{-1} vs 27 Kcal mole^{-1}). Char formation was attributed to this

stability. Under this condition, the formation of all major products were suppressed. The self-ignition temperature was also increased from 370°C for neat PI to 475°C for VPI.

Introduction

Much of the original action of flame retardation of polymers was in the field of plastics, and relatively little attention was paid to the flammability of elastomeric products. Even though the ignition and burning characteristics of rubbers were a matter of some concern in a few applications, the total volume of rubbers used in these applications was rather small and consequently, research in this subject lagged considerably behind the corresponding efforts attributed to plastics. The rapid increase in the use of elastomers in many consumer oriented applications has recently caused greater emphasis to be placed on the flammability behavior of these materials. The awakening interest in the flammability of elastomers is reflected in the sharp increase of studies on the subject over the past decade[1].

According to Fabris and Sommer[2], three approaches have mainly been used to prepare rubber compositions with decreased tendency to burn. The first approach involves compounding with flame retardant additives. The second involves copolymerization with small amounts of special comonomers and the third approach involves postreaction of the elastomer with specific reagents. A number of specific additive flame retardant formulations for elastomers including those for PI are reported by Trexler[3]. A typical non-flammable natural rubber composition consisted of 40-55 percent carbon black, 20-40 percent SiO_2, 20-30 percent chlorinated plasticizers,

4-8 percent calcium borate, 3-7 percent zinc borate, and 5-8 percent iron oxides[4].

In postreaction studies, Cockbain et al.[5,6] treated natural rubber swollen with trichlorobromomethane with high energy radiation or with a radical initiator. Addition of the halogens to the carbon double bonds resulted in products which retained their high elasticity. In a similar reaction, Rosin and Asscher[7] used carbon tetrachloride to react with 1,4 polybutadiene in the presence of $FeCl_3$ catalyst.

Among the comonomers claimed in the patent literature to impart flame retardation to rubbers were bis(2,3-dibromopropyl) fumrate[8], allyl or vinyl phosphates[9], monochlorostyrene[10], halogenated olefins[11], and vinylidene chloride[12]. The copolymers obtained were either used alone or compounded with additives such as phosphate plasticizer[8], Sb_2O_3[10], or alumina trihydrate[12].

Regardless of which approach to use, it should be emphasized that the factor of greatest importance when formulating flame retardant compositions is that none of the key physical properties of the rubber be impaired, although compromises between performance, burning characteristics and costs have to be considered.

The approach of postreaction was used in this work to flame-retard PI. About 1 percent pendant glycol groups were introduced to PI by controlled hydroxylation with peracetic acid. The polymer was then reacted with $VOCl_3$ to form a vanadium-coordinated polymer. The sample was examined for its behaviors in pyrolysis, oxidative pyrolysis, and ignition characteristics. Results obtained from neat PI under similar conditions were used for comparison.

Experimental

Sample Preparation

Natsyn 2200 (Goodyear) PI was purified by dissolving in toluene and precipitating with acetone. The polymer was then dried in vacuum. About 5 mg of the purified PI was dissolved in 300 ml of chloroform, and a solution consisting of 2 ml of chloroform, 2 ml of acetic acid, and 2 ml of peracetic acid was added dropwise to the solution. The use of acetic acid was to introduce micibility between chloroform and peracetic acid. The reaction was allowed tc run for 1C hours and base hydrolysis was performed by adding small amount of 1N NaOH and neutralizing the base with HCl. After 20 hours, the hydroxylated polymer was precipitated with acetone and vacuum dried. The infrared spectrum of this sample showed small OH stretching between 3300-3400 cm^{-1}, no carbonyl stretching was observed.

VPI was preoared by dissolving about 1 gm of the hydroxylated PI in 100 ml of dry chloroform and a solution consisting of 1 ml (10 mmole) of $VOCl_3$ (Alpha Products), 5 ml of chloroform, and 5 ml of carbon tetrachloride was added to the polymer solution. The latter solvent was used to aid solution between $VOCl_3$ and chloroform. The reaction was conducted under nitrogen in a glove box for an hour in the presence of P_2O_5 as drying agent. After the reaction, excess solvent was driven off by a Rotavapor (Brinkmann), the polymer, which was dark green in color, was then washed with dry carbon tetrachloride and vacuum dried at room temperature. Analysis of this polymer showed that it consisted of 3.4 percent by weight of vanadium and 3.09 percent of chlorine. The polymer was self-extinguishing in air when ignited.

Pyrolysis in Inert Atmosphere

TGA and pyrolysis of VPI were performed in a similar manner as described for PI in Chapter VII. About 4 mg of sample was used in each pyrolysis experiment. The polymer was pyrolyzed at 340°, 362°, and 384°C for different periods of time at each temperature. The products were similarly collected and pyrograms obtained by temperature programmed gas chromatography. The products (up to C_{16}) were similar to those found for PI and their relative distributions were examined.

The pyrolysis process followed first-order reaction kinetics. The rate constants of decomposition and the activation energy were compared to those obtained for PI.

Oxidative Pyrolysis

TGA and oxidative pyrolysis of VPI were performed in a similar manner as described for PI in Chapter VIII. About 5 mg of VPI was used in each pyrolysis experiment. The polymer was pyrolyzed at 315°,340°, and 362°C for different periods of time at each temperature. The products were similarly collected and pyrograms obtained by temperature programmed gas chromatography and again they were similar to those found for PI. DTA of this sample in air at a flow rate of 60 ml min^{-1} and a heating rate of 30°C min^{-1} was also examined.

The pyrolysis process followed first-order reaction kinetics. The results of kinetic studies were compared to those of neat PI. The absolute product distributions(calculated from areas under gas chromatographic peaks) of VPI and PI were compared as a function of temperature.

Results

Pyrolysis in Inert Atmosphere

Figure 1 shows the TGA curves in nitrogen for VPI and PI. Table 1 compares the relative concentrations of the products from the pyrolysis of VPI and PI in helium at 362°C(3 min). The relative weight percent of each product was calculated by normalizing the respective peak area to the sum of the areas of all of the volatiles. Figure 2 compares the rates of pyrolysis of VPI and PI in helium at indicated temperatures. The corresponding first-order kinetic semilog plot and Arrhenius plot are shown in Figures 3 and 4. The results of the kinetic studies of the pyrolysis of VPI and PI in helium are compared in Table 2.

Oxidative Pyrolysis

Figure 5 compares the TGA curves in air for VPI and PI. Figure 6 shows the corresponding weight loss as a function of temperature. The DTA of VPI in air is shown in Figure 7. Figure 8 compares the rates of pyrolysis of VPI and PI in air at indicated temperatures. The corresponding first-order kinetic semilog plot and the Arrhenius plot are shown in Figures 9 and 10.

Table 3 compares the results of the kinetic studies of the pyrolysis of VPI and PI in air.

Table 1

Relative Product Distributions of the Pyrolysis of VPI and PI at 362°C (3 min)

Product	VPI	PI
Methane	0.03	0.01
Ethylene	0.1	0.03
Ethane	0.02	0.01
Propylene	0.1	0.05
Propane	0.04	0.01
Isobutylene	0.1	0.02
Butenes	0.09	0.02
Methyl butene	0.1	0.02
Isoprene	8.4	7.2
Toluene	0.06	0.03
2,3 dimethyl cyclopentene	3.7	1.5
Octene	0.2	0.05
2,4 dimethyl cyclohexene	0.5	0.14
m-xylene	1.7	0.4
1 methyl-4-ethyl cyclohexene	0.4	0.2
1,5 dimethyl-5-vinyl cyclohexene	4.4	5.1
Dipentene	77.0	85.0
$C_{15}H_{24}$ [a]	2.0	4.0
$C_{16}H_{26}$ [b]	1.7	1.2
unidentified	0.4	0.13

[a] 4 isomers

[b] 3 isomers

Table 2

Kinetic Results of the Pyrolysis of VPI and PI in Helium

	Rate Constants, sec^{-1}	
Temp. °C	VPI	PI
315	---	3.0×10^{-4}
340	1.2×10^{-3}	1.3×10^{-3}
362	4.2×10^{-3}	4.8×10^{-3}
384	1.1×10^{-2}	1.1×10^{-2}
Activation Energy, Kcal $mole^{-1}$	41	40

Table 3

Kinetic Results of the Pyrolysis of VPI and PI in Air

	Rate Constants, sec^{-1}	
Temp. °C	VPI	PI
268	---	4.0×10^{-4}
290	---	6.3×10^{-4}
315	7.0×10^{-5}	4.0×10^{-3}
340	4.4×10^{-4}	5.8×10^{-3}
362	1.7×10^{-3}	---
Activation Energy, Kcal $mole^{-1}$	50	27

The major products of the oxidative pyrolysis of VPI and PI in this work were ethylene, ethane, propylene, acetone, acetaldehyde, butan-1-al, methyl vinyl ketone, and methyl ethyl ketone. The absolute amount of each of these products, as measured from the area under peak, from VPI was normalized with respect to its corresponding peak from PI. Therefore, a ratio of one means the same amount of the same product are produced from both materials. Fractional quantities indicate suppression of products by VPI. Figure 11 shows the absolute normalized distributions of the above products (except methyl ethyl ketone) between 315°-362°C.

Discussion of Results

The reaction of organic peracids with unsaturated compounds, originally discovered by Priheschajew[13], is general for compounds with isolated double bonds. The reactivity of a given olefinic material with a peracid depends on the specific peracid employed and the nature of substituted groups neighboring the double bond. The reaction mechanism had been elucidated by Swern[14]. It proceeds by cis addition of an oxygen atom to the double bond to form an oxirane intermediate and then the corresponding hydroxyacetate. Hydrolysis of the latter yields the desired dihydroxy compound. The reaction conditions for the hydroxylation are prolonged reaction periods in the presence of acid or base catalyst[15,16].

In this work, 0.2 ml of an acetic acid solution containing 40 percent peracetic acid was used to hydroxylate PI. Theoretical calculation basing on one mole of acid per mole of monomer indicates that this corresponds to about 1.5 percent hydroxylation of the polymer sample. Attempts to quantitatively determine the degree of hydroxylation were not successful.

There have been a lot of studies on the effect of metals on the thermoxidative stability of rubbers. Lee et al.[17] had reported that at 110°C, the strongest catalysts for the thermoxidative degradation of rubbers were stearates of Co and Mn. These authors concluded that: metals with one electron transfer during the redox reaction such as Co, Cu, Mn, Ce, and Fe are more reactive; metals with two electron transfer such as Pb and Sn are less reactive and; metals with no electron transfer such as Zn and Na are normally not active. These authors also cautioned that the above metals would behave differently in pyrolysis.

Mayo et al.[18] reported the effect of soluble transition metal salts on the oxidation of PI at 50°C and again salts of Co and Mn were among the most active catalysts. The catalytic effect of Ti compounds in decreasing the thermoxidative stability of PI was reported by Augert et al.[19]. According to these authors, the catalytic activity of the Ti compounds was greater than that of Fe and was about the same as that of Cu compounds.

At the other end of the spectrum, the inhibitive effect of metals on organic systems was reported by Horowitz[20]. According to this author, the chemical combination of metal ions with organic molecules such as 8-hydroxyquinoline and derivatives of bis(8-hydroxyquinoline) led to coordination complexes or oligmers with enhanced thermal and thermoxidative stabilities. The stability of these compounds depends on the central metal and also on the nature of the ligand. The order of the thermal stability in vacuo of these metallo-organic systems was Mn > Co > Ni > Cu. Under thermoxidative conditions, the order of stability was reversed.

It is also possible to stabilize preformed organic polymers provided they are synthesized to have functional groups so positioned strategically as side chains that can be reacted with metal ions to form coordinated structures. Such an example was again illustrated by Horowitz[20] who reported that the polymer prepared from salicyaldehyde and butylene mercaptan, when reacted with a divalent, first-row transition metal having a coordination number of 4 yielded a metallo-organic system with improved stability.

Drinkard[21] studied some of the polymers formed through the above metallization process and found that the Zn polymer was more stable than the Cu polymer. Aliwi and Bamford[22,23] reported the preparation of coordination photoactive polymers by introducing vanadium chelate residues into preformed polymer molecules with pendant hydroxyl groups. However, no stability study was attempted.

In this work, the thermal stability of VPI and PI in inert atmosphere was about the same and as a result, both polymer samples acquired an activation energy of pyrolysis of about 40 Kcal mole^{-1}. VPI showed a slight weight loss at temperatures below 200°C, this is believed to be due to entrapped solvents. This polymer also left a 5 percent sooty residue at 500°C. This is probably due to residual oxygen, either in the apparatus system or in the polymer itself. The resulting vanadium oxides, like chromium oxides, are good dehydrogenation catalysts[24].

It should be pointed out that while the thermal stability of VPI and PI was very similar in inert atmosphere, their product distributions, however, were very different. At 362°C, the volatiles (up to C_{16}) from VPI were only 30 percent of those from PI. This indicated that the

vanadium-containing polymer formed less low-boiling products than neat PI. The weight percent of each product in Table 1 is only a relative figure and represents the relative concentration of that product in the volatiles.

In oxidative environment, vanadium inhibited pyrolysis by in-situ char formation. This was reflected by lower rates of decomposition and a higher activation energy compared to those of PI (50 Kcal $mole^{-1}$ vs 27 Kcal $mole^{-1}$). Under similar conditions, the temperatures for 50 percent weight loss for VPI and PI were 420° and 360°C respectively. DTA showed that VPI ignited at about 475°C and under similar conditions, PI ignited at about 370°C (Chapter VIII). Two minor DTA ignition exotherms occurring at 350°C and 400°C respectively, were also observed for VPI. This is believed to be due to the inhomogeneous distributions of vanadium in the polymer.

TGA in air showed that VPI left an 8 percent char at 450°C and this char was stable up to 600°C. The behavior of this char at still higher temperatures was not investigated. Finally, under oxidative conditions, the formations of all major products were suppressed (Figure 11). The relative amounts of major oxygenates remained about the same throughout the temperature range studied.

Conclusion

Vanadium oxytrichloride($VOCl_3$) was used to react with PI which was hydroxylated with controlled amount of peracetic acid. The final product was elastic and self-extinguishing in air when ignited. The metal-containing polymer was investigated for its thermal stability and ignition characteristics by TGA and DTA. The pyrolysis and oxidative pyrolysis of the metal-containing polymer were found to follow first-order reaction kinetics. The rates of decomposition and the corresponding activation energies were compared to those obtained for PI.

In inert atmosphere, the thermal stability of the metal-containing polymer was very similar to that of the neat polymer. As a result, both samples acquired about the same activation energy of pyrolysis, i.e., 40 Kcal $mole^{-1}$. Product distributions, however, were very different between the two polymers. The metal-containing polymer was found to form less volatiles separable by gas chromatography.

In oxidative environment, the metal-containing polymer was more stable than neat PI. The former polymer formed char resulting in lower rates of decomposition and higher activation energy(50 Kcal $mole^{-1}$ vs 27 Kcal $mole^{-1}$). Under this condition, the formations of all major products were suppressed. The self-ignition temperature in air was also increased from 370°C for the neat polymer to 475°C for the metal-containing sample.

Acknowledgment

The author would like to acknowledge the help of B. McNamara in preparing the vanadium polymer.

References

1. Johnson, P.R., Pariser, R., McEvoy, J.J., Rubber Age, 107,29, 1975
2. Fabris, H.J., Sommer, J.G., Rubber Chem.Technol., 50, 523,1977
3. Trexler, H.E., Rubber Chem. Technol., 46, 1114, 1973
4. French Pattern 7,016,133; Chemical Abstracts, 77, 6987p
5. Cockbain, E.G., Pendle, T.D., Pole, E.G., Turner, D.T., Proceedings of the 4th Rubber Technology Conference, Messenger, T.H., Ed., Institution of the Rubber Industry, London, 498, 1963
6. Cockbain, E.G., Pendle, T.D., Turner, D.T., Chem. Ind. (London), 318, 1960
7. Rosin, H., Asscher, M., J. Appl. Polymer Sci., 13, 1721, 1969
8. Cummings, W., (to U.S. Rubber Co.), U.S. 3,260,772, (July 12, 1966)
9. B.F. Goodrich Co., Belgian 720,954 (March 3, 1969)
10. Dow Chemical Co., Technical Bulletin, 'Monochlorostyrene in Fire Retardant Foam Rubber'
11. Standard Brands Co., Belgian 729,226 (Feb. 28, 1969)
12. Polymer Corp., Australian 32,843/68 (Aug. 7, 1969)
13. Pribeschajew, H., Chem. Ber., 42, 4811, 1909
14. Swern, D., 'Organic Reactions', 7, 383, Wiley, N.Y.
15. Fettes, E.M., 'Chemical Reactions of Polymers', 152, Intersciences, N.Y.
16. Swern, D., J. Am. Chem. Soc., 70, 1235, 1948
17. Lee, L.H., Stacy, C.L., Engel, R.G., J. Appl. Polymer Sci., 10, 1699, 1966
18. Mayo, F.R., Egger, K., Irwin, K.C., Rubber Chem. Technol., 41, 271, 1968

19. Augert, L.G., Andreeva, A.I., Kuzminskii, A.S., Vysokomol. Soedin., A. 10, 580, 1968; 12, 2046, 1970

20. Horowitz, E., 'Stabilization of Polymers and Stabilizer Process', ed. Gould, R.F., Advances in Chemistry Series, 85, 82, 1968

21. Drinkard, W.C., Jr., WADC Tech. Report 59-427, 367 (Jan. 1960)

22. Aliwi, S.M., Bamford, C.H., J. Chem. Soc., Faraday Trans. I., 71, 52, 1733, 1975

23. Aliwi, S.M., Bamford, C.H., Polymer, 18, 375, 1977

24. Kent, J.A., ed., 'Handbook of Industrial Chemistry', 417, Reinhold, N.Y., 1974

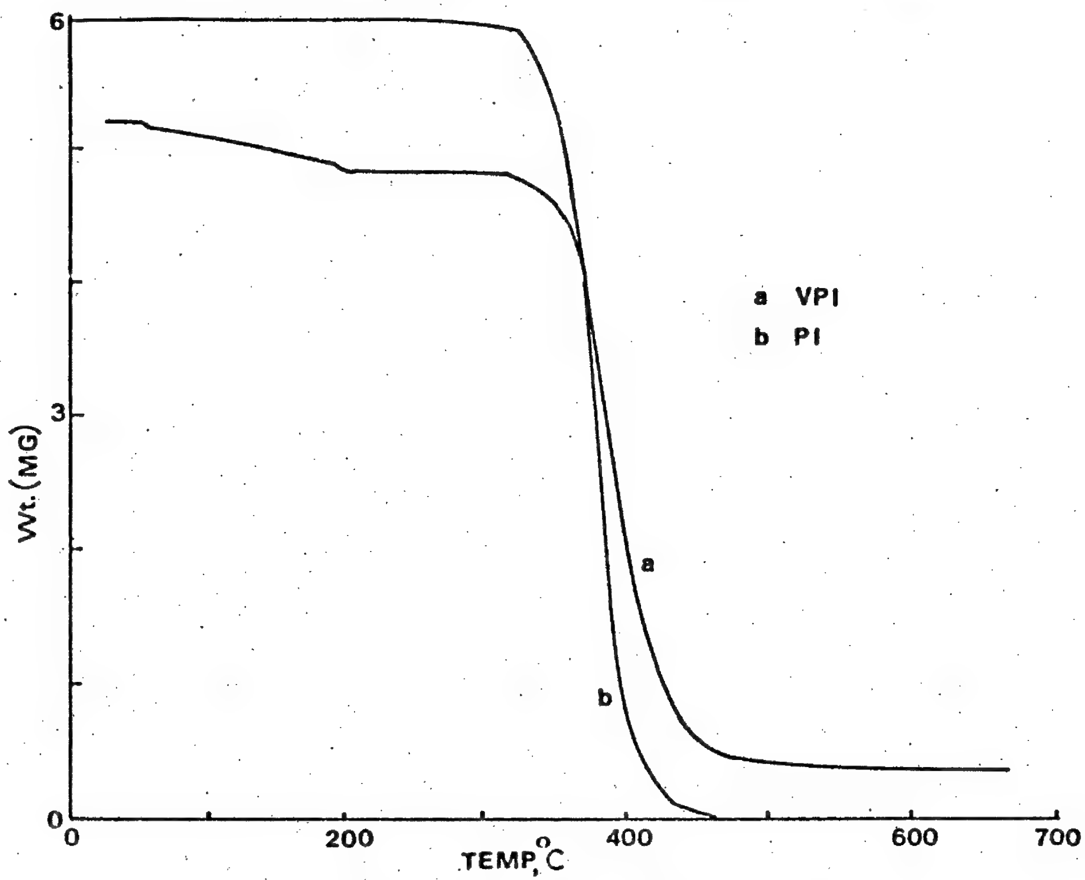


Fig. 1 TGA thermograms of VPI and PI in nitrogen

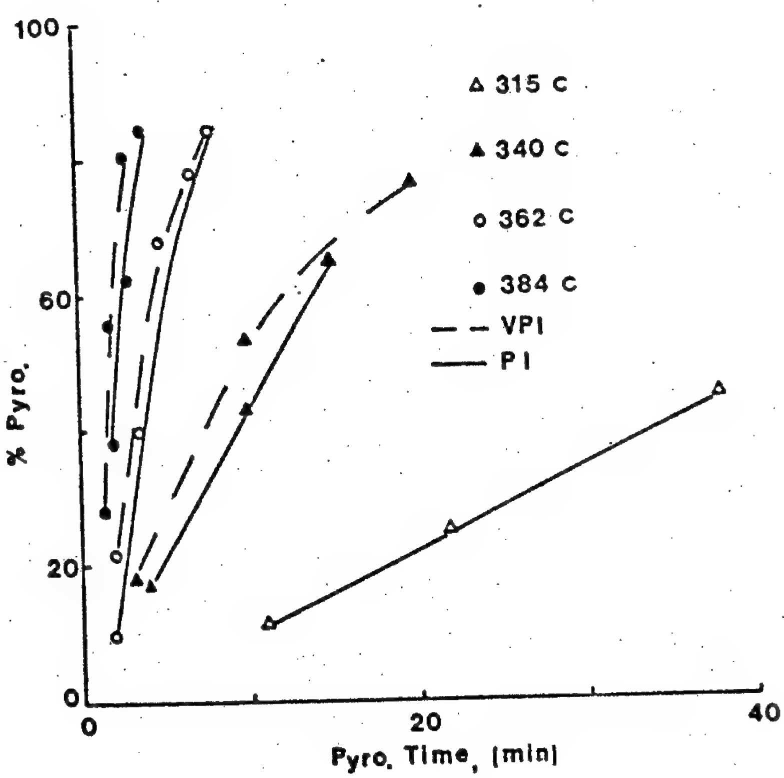


Fig. 2 Rates of pyrolysis of VPI and PI in helium at indicated temperatures

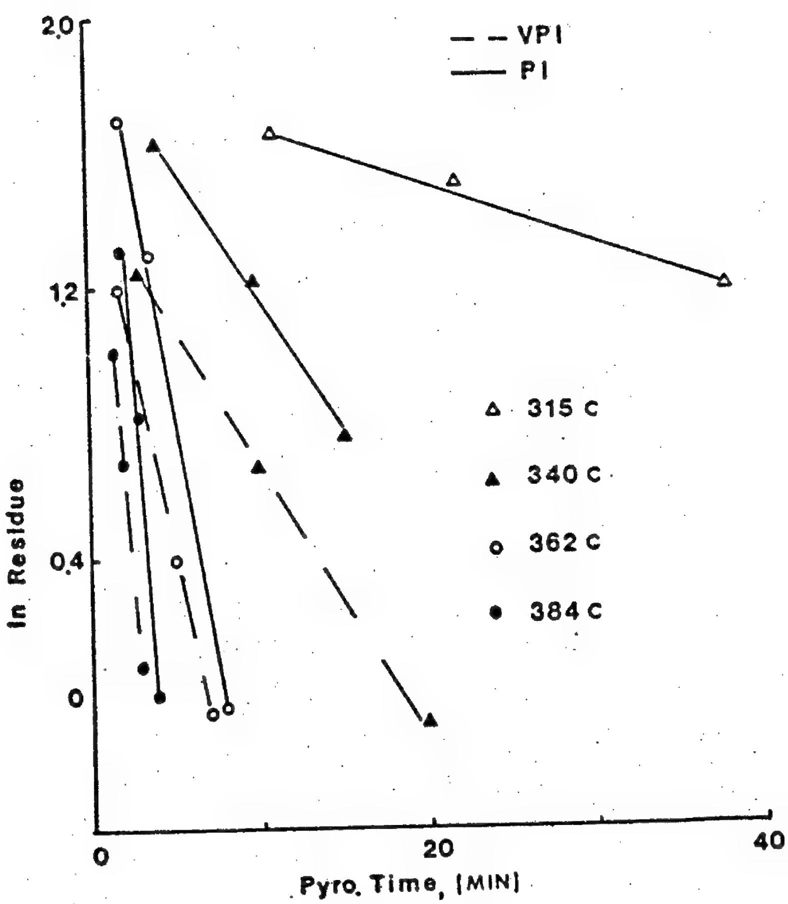


Fig. 3 First-order kinetic semilog plot for pyrolysis of VPI and PI in helium at indicated temperatures

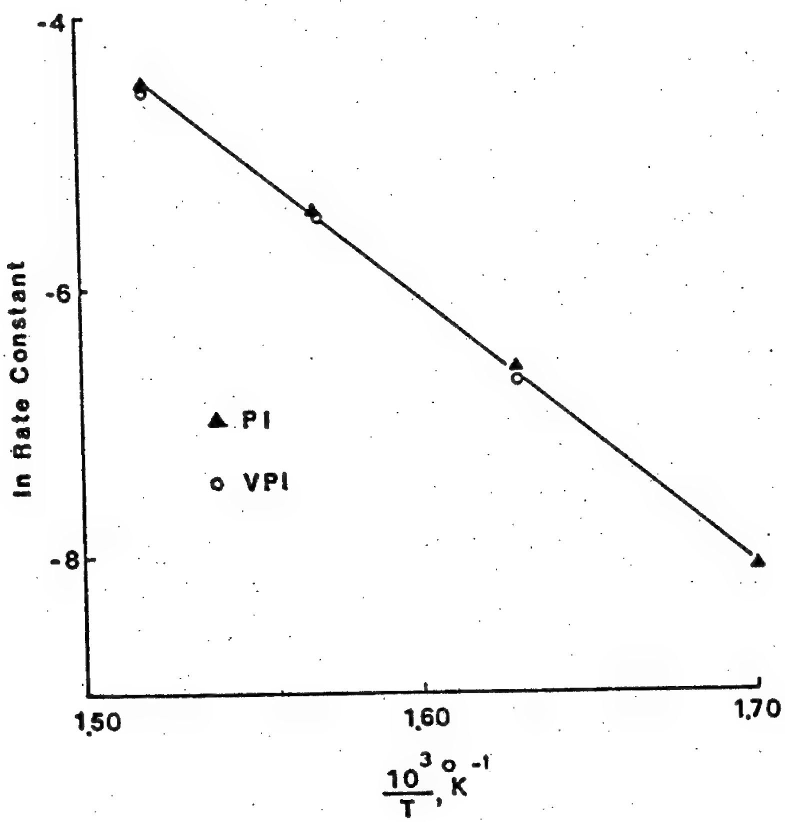


Fig. 4 Arrhenius plot for pyrolysis of VPI and PI in helium

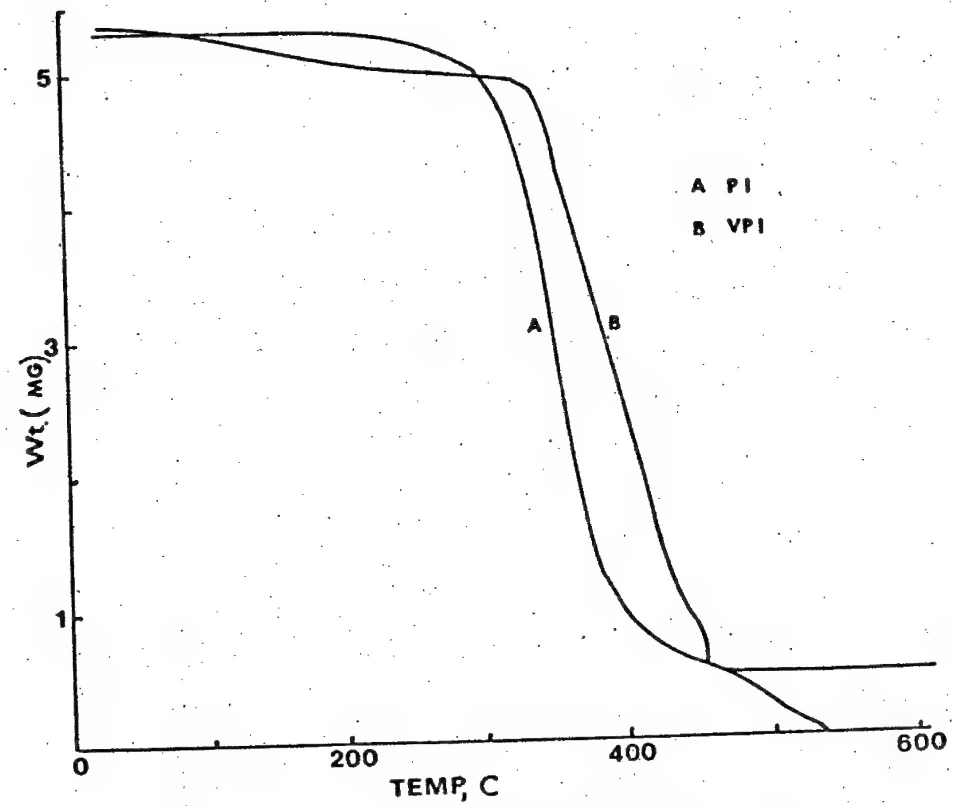


Fig. 5 TGA thermograms of VPI and PI in air

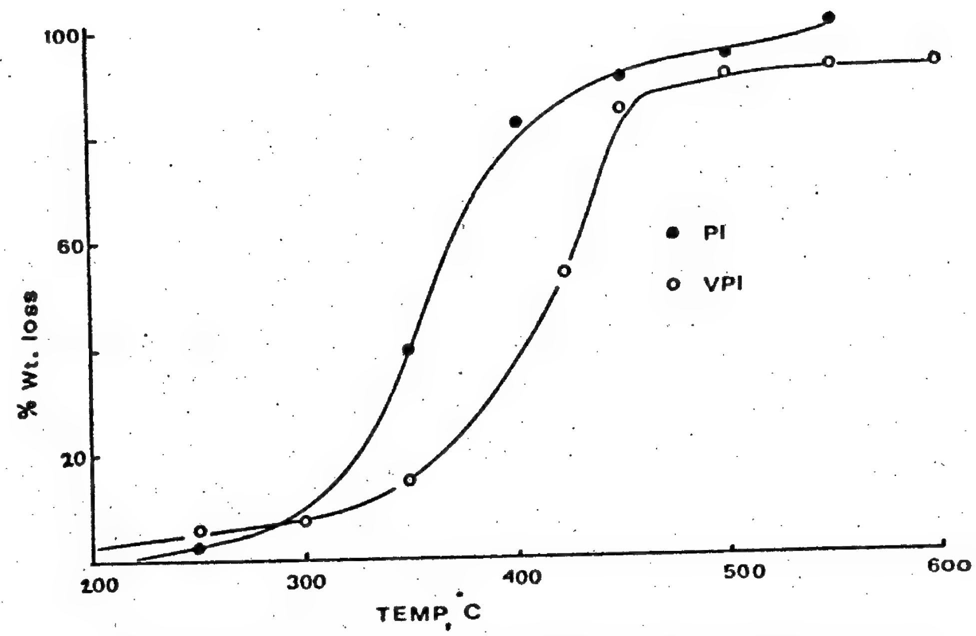


Fig. 6 Percent weight loss of VPI and PI in air as a function of temperature

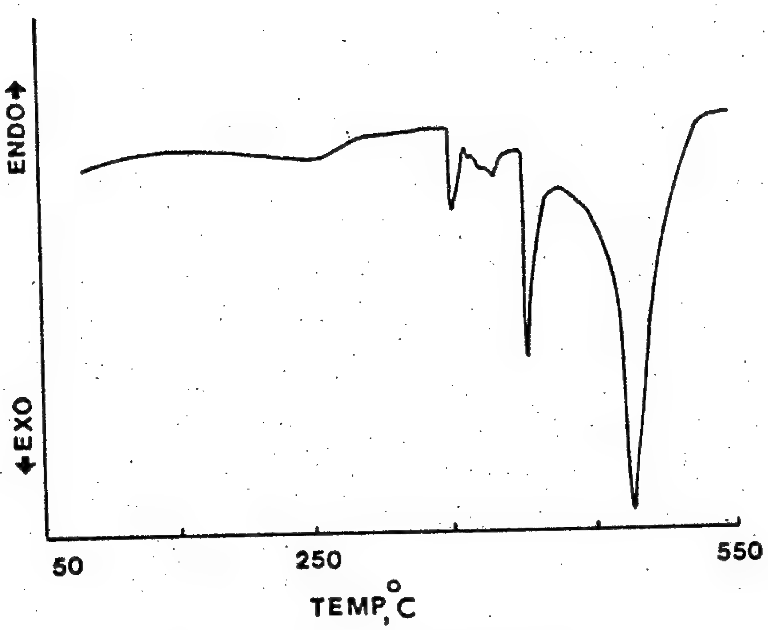


Fig. 7 DTA thermogram of VPI in air

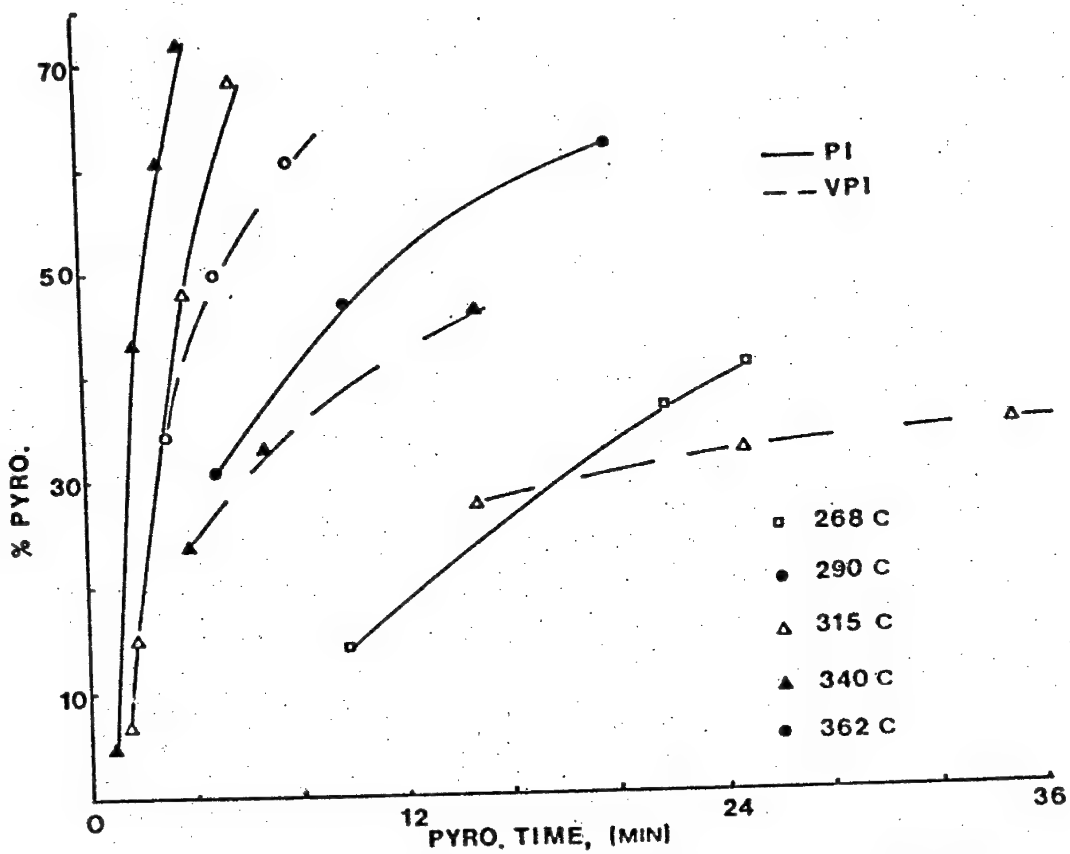


Fig. 8 Rates of pyrolysis of VPI and PI in air at indicated temperatures

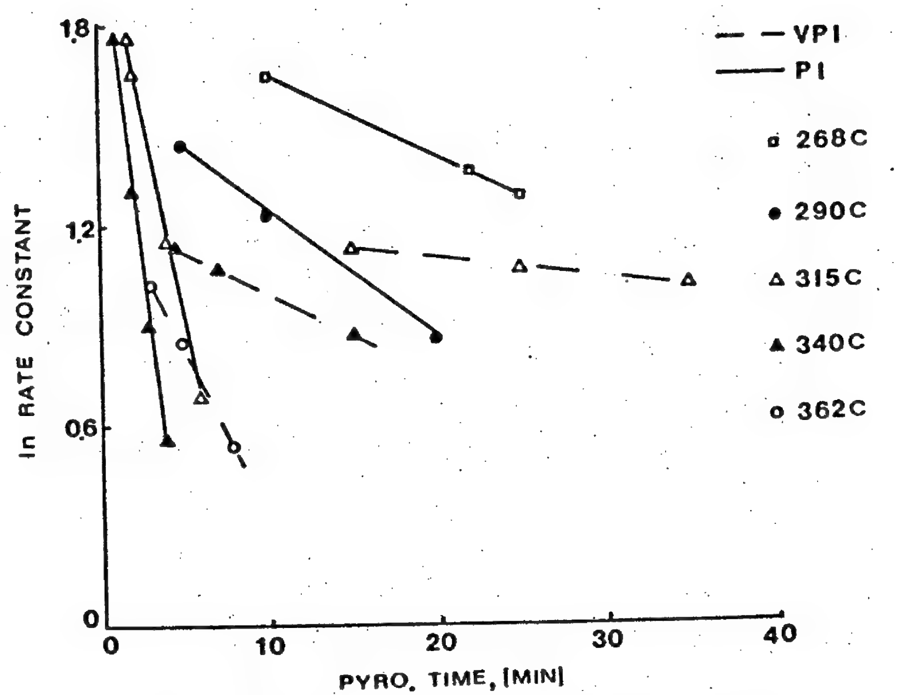


Fig. 9 First-order kinetic semilog plot for pyrolysis of VPI and PI in air at indicated temperatures

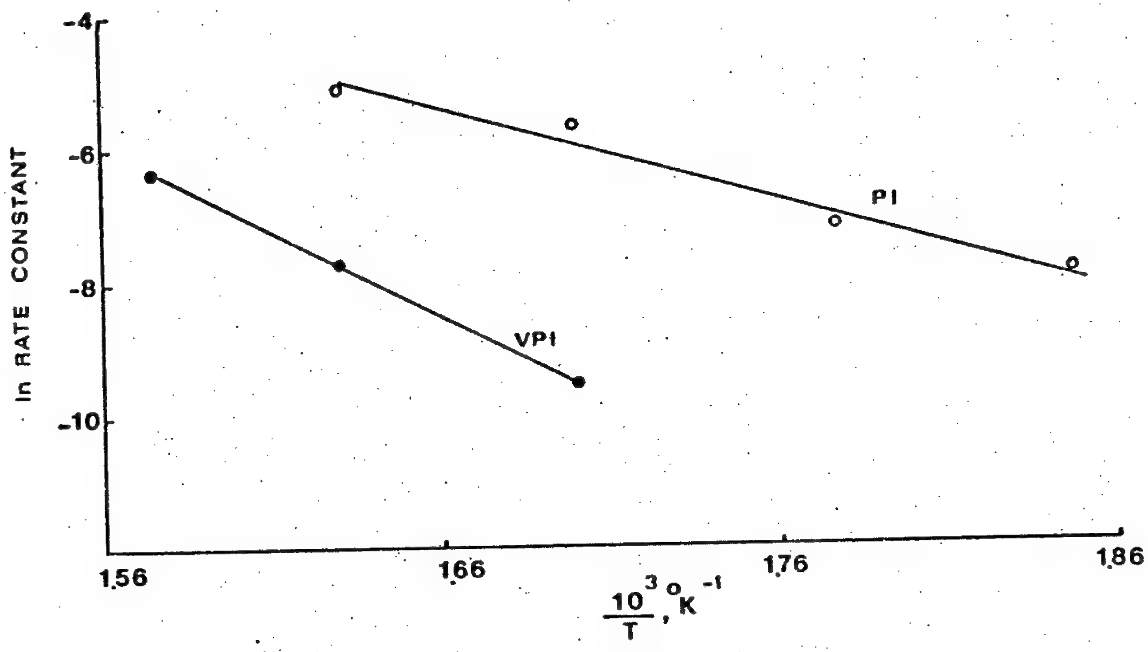


Fig. 10 Arrhenius plot for pyrolysis of VPI and PI in air

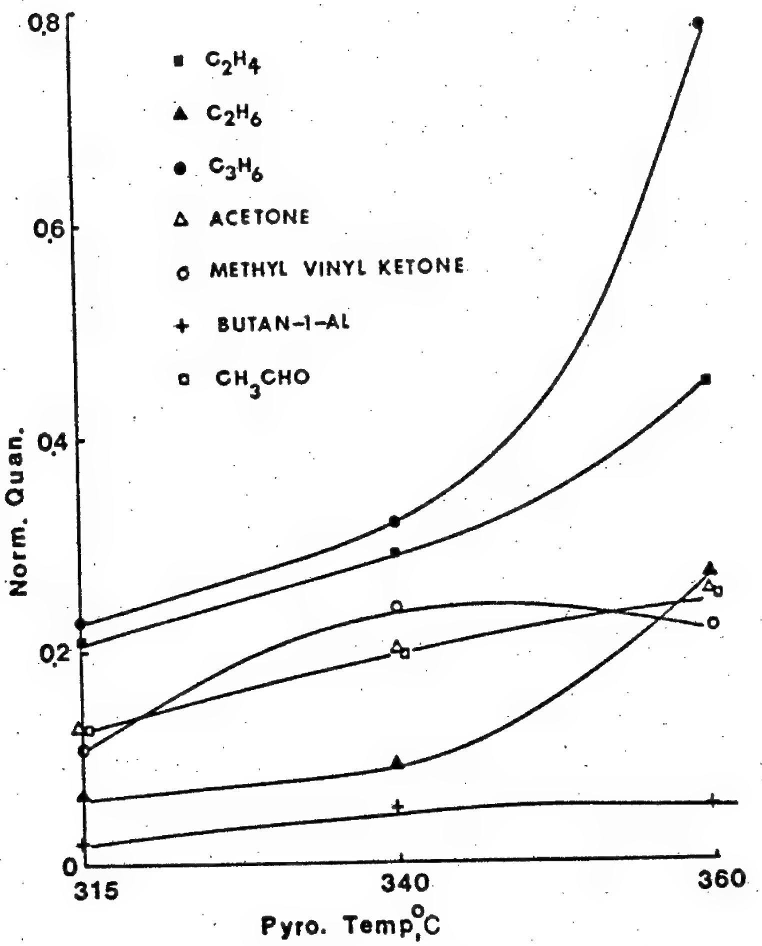


Fig. 11 Absolute normalized distributions of major products from pyrolysis of VPI and PI in air as a function of pyrolysis temperature

CHAPTER X

CONCLUSION

Polymer flammability has become an important social and scientific problem; it deals with our basic everyday life situations, from housing, transportation to clothing and so on. The motive for the development of flame retardant polymeric materials is the result of sociological pressure and legislation.

A simplified picture of a burning polymer may be thought of as involving two distinct processes. One is the 'volatilization' of the solid polymer into combustible gaseous products and the other is the combustion of these products in the surrounding oxygen-containing environment. Presumably, under steady-state conditions, heat from the flame accompanying the second process is conducted back to the solid or molten polymer thereby causing the formation of a continuous and steady supply of 'fuels'. To inhibit the overall combustion process by either slowing down the 'volatilization' of the solid polymer or by retarding the oxygen-supported combustion in the vapor phase, are in principle possible. Chemical and physical methods of inhibiting the above processes had been discussed by Cullis[1].

The primary interest in this study is the inhibition of the solid phase by slowing down the 'volatilization' of the molten polymer so that less 'fuels' are available for combustion. With regard to the 'volatilization' of the polymer, whether the decomposition process is pure pyrolysis or oxidative pyrolysis is still largely unsettled. Some workers believe that simple thermal decomposition without the interven-

tion of oxygen is responsible for the production of gaseous products. Then the process is dependent entirely on the chemical nature of the polymer and on the pyrolysis temperature. Some polymers will undergo chain scissions, while other polymers might undergo unzippings if their ceiling temperatures are well below the pyrolysis temperature. On the other hand, other workers believe oxygen is involved so that the process is in fact a thermoxidative decomposition.

In this study, the oxidative pyrolysis of polypropylene and polyisoprene were found to occur at lower temperatures than the corresponding pure pyrolysis. The activation energies for the oxidative pyrolysis were also much lower than those for pure pyrolysis. When the oxidative pyrolysis of polypropylene was studied as a function of oxygen concentration, similar products were formed from 1 percent to about 60 percent oxygen although the formation of products was diffusion controlled. An increase of oxygen concentration increased the rate of oxidative pyrolysis but not the corresponding activation energy as evidenced by the pyrolysis of the chromium-containing polypropylene in air and in pure oxygen. This leads to the belief that the activation energy at 1 percent oxygen should not be too different from those at higher oxygen concentrations especially when at 1 percent oxygen, an average of 30 percent of each of the major products from the oxidative pyrolysis of polypropylene had already been formed. Hence, when a polymer is burning in air, it is conceivable that oxidative pyrolysis, being favored kinetically, contributes predominantly to the liberation of combustible volatiles from the polymer.

The effectiveness of chromium and vanadium metal compounds as potential flame retardants had been elucidated in this study. They inhibited oxidative pyrolysis resulting in the liberation of less volatile 'fuels' to support combustion and were capable of increasing the self-ignition temperatures of the polymers. The role of chlorine in the solid phase is unclear, it is possible that it existed as a synergist in the above systems. Synergistic systems of metal chelates with halogenated compounds had been reported in patent literatures[2,3].

Mark et al.[4] had established a number of guidelines for an ideal flame retardant polymer system. This system should have a high resistance to ignition and flame propagation; a low rate of pyrolysis; a low rate and amount of smoke generation; low combustibility and toxicity of volatile gases; retention of reduced flammability during use; acceptability in appearance and properties for specific end-uses and; little or no economic penalty. All of these requirements dictate the type of evaluation necessary for flame retardant systems. Many of these guidelines such as smoke generation and end-use property studies have not been addressed upon in this study. Finally, the behaviors of other transition metal compounds as potential flame retardants need to be studied in order that progress continue in this area.

References

1. Cullis, C.F., Oxidation and Combustion Revs., 5, 83, 1971

2. Rauschenback, R.D., Naarmann, H., Meyer, F., Ilgemann, R., (to Badische Anilin & Soda-Fabrik AG), U.S. Pat. 3,326,832 (1967)

3. Berridge, C.A., (to General Electric Co.), U.S. Pat. 3,154,515 (1964)

4. Mark, H.F., Atlas, S.M., Shalaby, S.W., Pearce, E.M., Polymer News, 2, 3, 1976